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AMINO HYDROXY NAPHTHALENE SULPHONIC ACIDS

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Bachelor of Philosophy

Chemistry Discipline

1985


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ABSTRACT

AMINO HYDROXY NAPHTHALENE SULPHONIC ACIDS

This review of the preparation and possible manufacture of the 84 isomeric Amino Hydroxy Naphthalene Sulphonic Acids, has been written on the basis that it was a very specialised subject made more so, by directing it from a commercial angle. To this end, naming of the compounds, their uses in the dyestuff field, and methods of preparation have been summarised at length to enable the literature survey to be readily meaningful.

The survey has been made not only from available literature, but also from private information available to the Author. These sources have revealed that from 1953 - 1982, of the isomers known, only 40 have been mentioned in the review period, and only 17 with a method of preparation. Information on 8 new isomers was also found, and methods of preparation of 4 of these. Methods of preparation for the other 4 have been suggested.

New methods for the synthesising some of the isomers have been found, and as laboratory methods they have a definite value, but do not appear to the Author to have a potential commercial future and this is confirmed by the absence of further information.

The review has revealed a decline in the use of these compounds, and reasons have been suggested for this downward movement.

Of the five manufactured isomers in 1953, only 3 now appear to be made, and their processes have been changed due to environmental aspects. Methods for the preparation of 20 unknown isomers have been suggested with comments where appropriate, and 5 unknown isomers have been prepared in the laboratory.

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1.0 Introduction

The purpose of this review can be defined in the following manner:-

"To investigate the preparation and manufacture of Amino Hydroxy Naphthalene Sulphonic Acids during the period 1953 - 1982; to suggest schemes for the preparation of the unknown isomers and examine critically changes in manufacturing procedures."

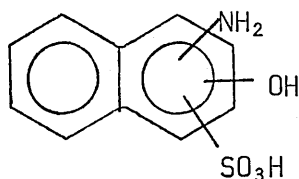
This will be systematically discussed as follows:-

- (1) A record of all the indexed Amino Hydroxy Naphthalene Sulphonic Acids.
- (2) Information on the preparation of isomers prior to 1953.
- (3) Methods of preparation of isomers prepared post 1953.
- (4) Information on the isomers which had been manufactured.
- (5) Suggested methods of preparation for the unknown isomers.

1953 has been chosen as the starting date because Thorpe's Dictionary and Donaldson's 'Chemistry of Naphthalene Compounds' review the literature to about that year.

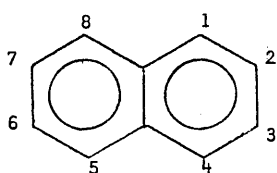
1.1 Nomenclature

Amino Hydroxy Naphthalene Sulphonic Acids have been investigated and used in the manufacture of Azo Dyestuffs for about 100 years. These compounds can be represented by the general formula:-

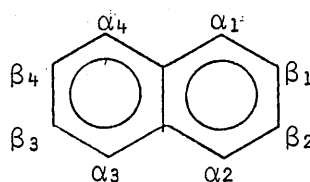


which represents the 84 possible isomers.

The naphthalene ring may be designated in two different ways:-



or

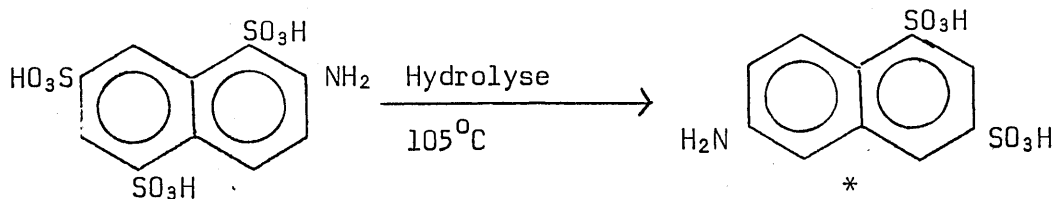


but only the numbered one is in use today. During the last century the system of nomenclature of these compounds has changed twice; initially the Amino group was numbered 1, or 2, and the Hydroxy-Naphthalene called Naphthol thus giving the name of Amino Naphthol Sulphonic Acid which is still widely used. Some sixty years later, the Naphthol was designated as the dominant group, and was numbered 1, or 2. It was therefore possible to have 14 sets of Naphthol-Sulphonic Acids with six different amine isomers. Now the Sulphonic acid has been designated as the dominant group and the

compounds are known as Amino Hydroxy Naphthalene Sulphonic Acids. Literature reports are not all consistent with the last system, but it will generally be used in this review except when directly quoting from the literature, when the rings will be numbered. This last system has created problems in presenting reactions involving naphthalene-sulphonic acids as is shown by the following statement:-

"When 2-amino-naphthalene-1,5,7-trisulphonic acid is heated in 50% sulphuric acid at 105°C, the 1-sulphonic acid group is removed leaving 6-amino-naphthalene-1,3-disulphonic acid."

To show this re-orientation of the molecule to fit the numbering system the ring has been 'Starred' * as below.



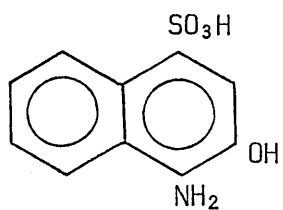
1.2 Historical Aspect

The two main sources of information on these compounds are Thorpe's Dictionary¹ and Donaldson's 'Chemistry of Napthalene Compounds'². These review the information up to 1953; and record that 51 isomers had been synthesised, but only 5 had reached the manufacturing status. These five will be referred to henceforth as 'The Big Five'. Information from private sources showed that at least 14 more of the 51 isomers were systematically examined as potential sales products but never achieved that status. Thus 33 isomers remained unrecorded in 1953.

Many Napthalene compounds have been given names of their discoverer e.g. Cleve or Dahl, or an alphabetical letter. These have been used throughout the world as a simple means of identification, and possibly far more important as a safety measure in the marking of containers in the industrial field. These trivial names will be given in this review because it is easier for the reader to identify compounds by this means.

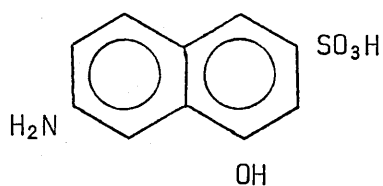
1.3 The Identity of the 'Big Five'

(a)



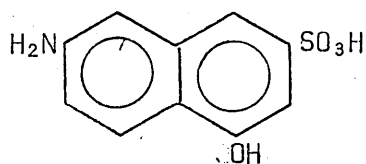
4-amino-3-hydroxynaphthalene-1-sulphonic acid (1:2:4 Acid)

(b)



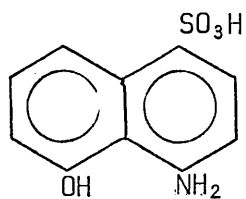
6-amino-4-hydroxynaphthalene-2-sulphonic acid (Y Acid)

(c)



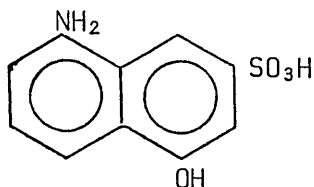
7-amino-4-hydroxynaphthalene-2-sulphonic acid (J. Acid)

(d)



4-amino-5-hydroxynaphthalene-1-sulphonic acid (S. Acid)

(e)



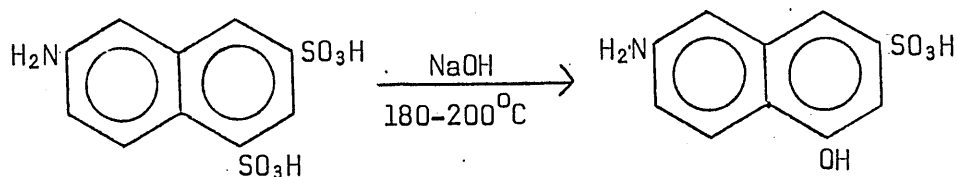
8-amino-4-hydroxynaphthalene-2-sulphonic acid (M. Acid)

M. Acid has only been manufactured in Germany.

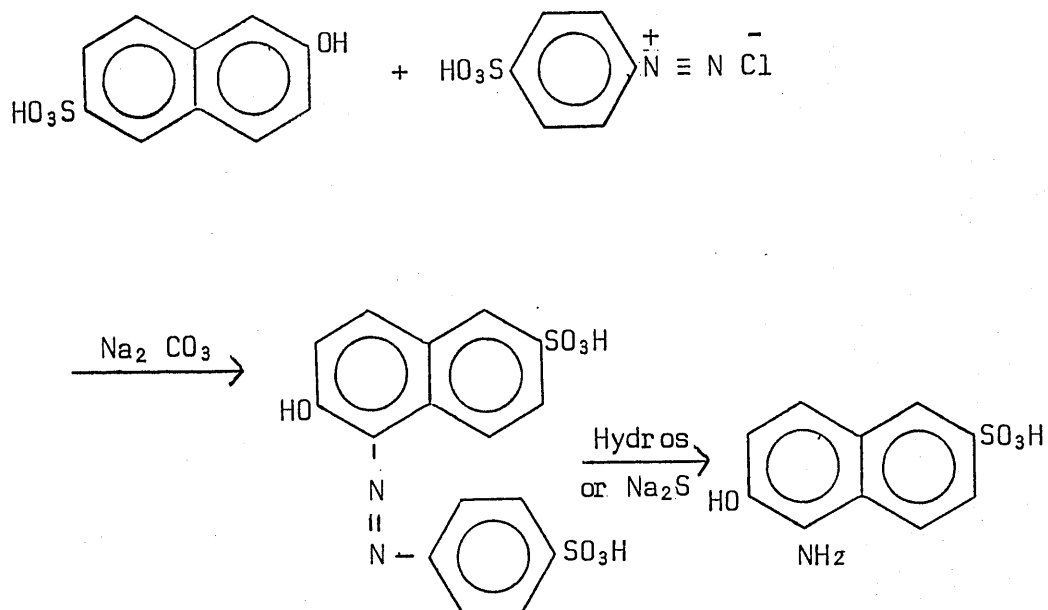
1.4 Methods of Preparation of Amino Hydroxy Naphthalene Sulphonic Acids

The following methods are normally used for the preparation of these compounds and with the exception of (j) have all been used industrially by the Author.

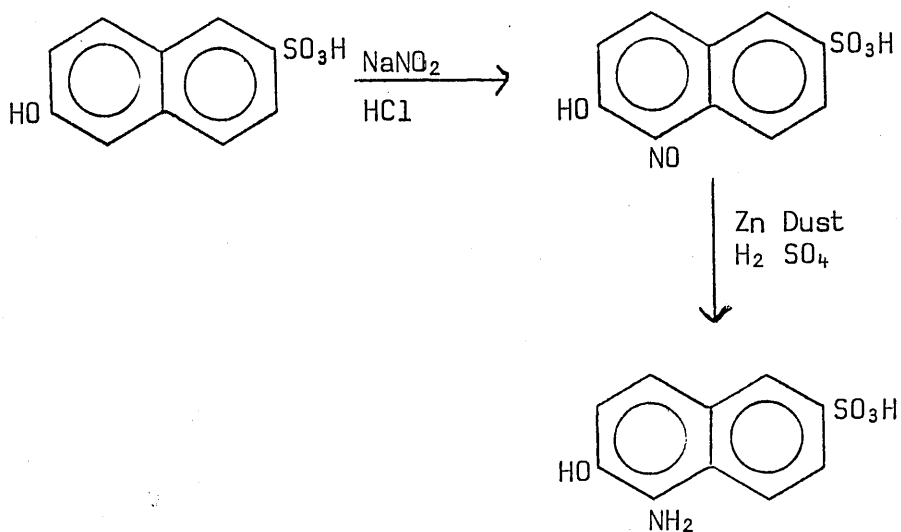
- (a) By Alkali fusion of a naphthylamine-disulphonic acid at about 200°C.



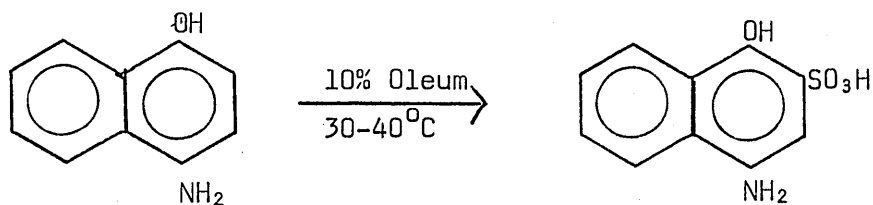
- (b) By coupling a naphthol-sulphonic acid with a diazo compound to form an azo dyestuff and reduction of the dyestuff.



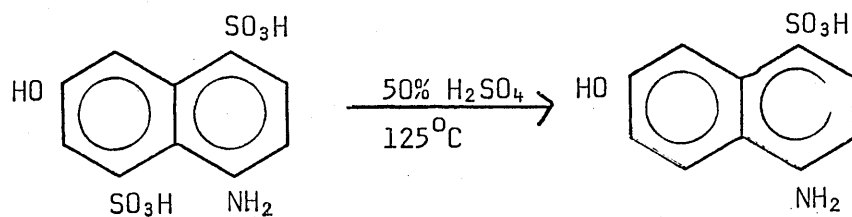
- (c) Nitrosation of a naphthol-sulphonic acid and reduction of the resultant nitroso compound.



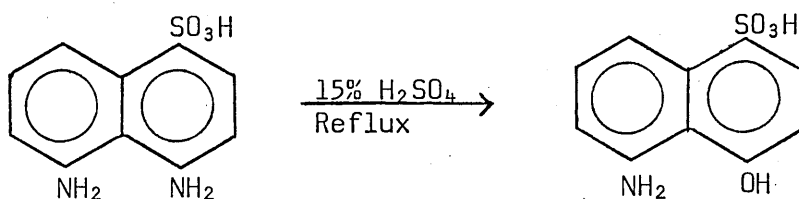
- (d) Sulphonation of an amino-naphthol.



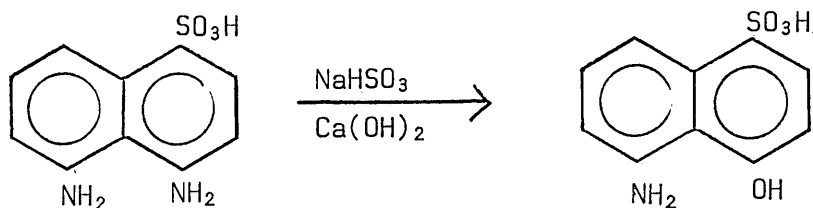
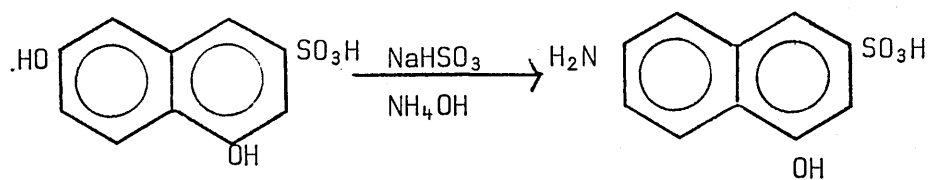
- (e) Desulphonation of an amino-naphthol-disulphonic acid.



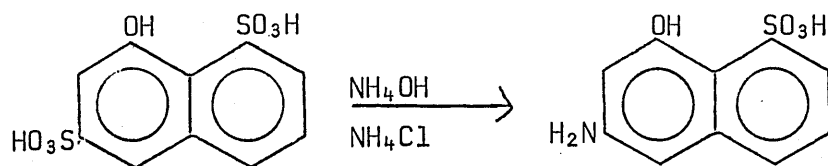
- (f) From 1,8-diamino-naphthalene-sulphonic acid by hydrolysis.



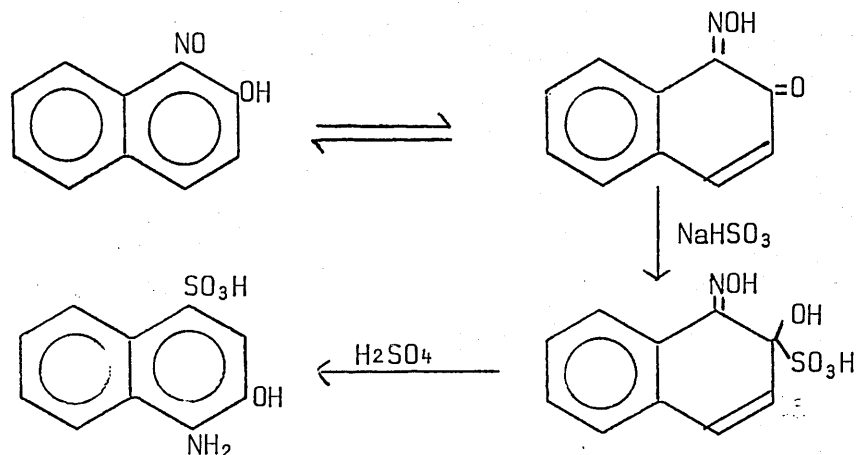
- (g) Bucherer Reaction of an 'OH' or 'NH₂' group by means of sodium bisulphite.



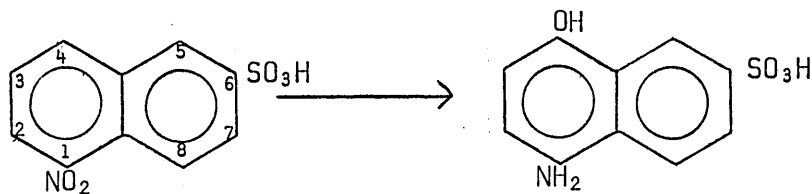
(h) A 1-naphthol-disulphonic acid with a sulphonic acid group in the 3-position will exchange it for an amino group on heating with ammonia and ammonium chloride at 180°C under pressure.



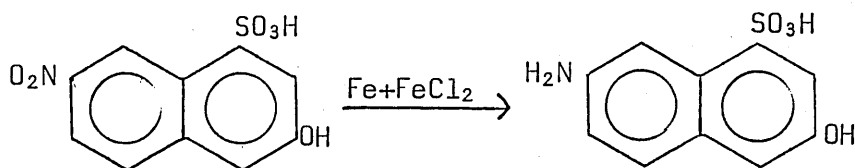
(i) The re-arrangement of a nitroso-naphthol.



(j) A 1-nitro-naphthalene-sulphonic acid having the two substituents in different rings, when reduced electrolytically in acid solution or with ammonium sulphide and followed by acidification are substituted in the 4-position by an 'OH' group.



(k) Reduction of a nitro-naphthol-sulphonic acid



1.4.1 Comment on the Methods of Preparation

Method (a) Before attempting this method of preparation, Friedleander's Rules of Fusion³ should be studied. These are:-

"(1) With 1-naphthol and 1-naphthylamine-sulphonic acids which have among others a sulphonic acid group in position-8, fusion gives 1,8-dihydroxy-naphthalene or 1-amino-8-naphthol-sulphonic acids respectively.

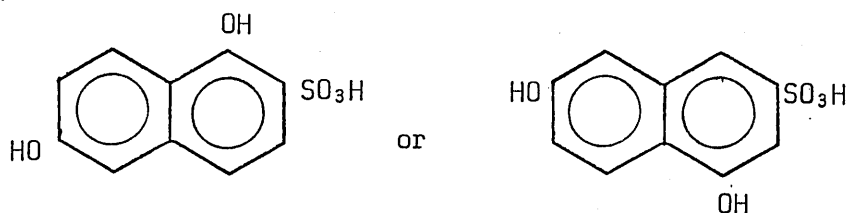
(2) In 1-naphthol and 1-naphthylamine-sulphonic acids, the sulphonic acid groups may be placed in the following order of resistance to hydrolysis, 8-5-6-7-3-2-4. The -2- and -4- sulphonic acid groups are so resistant that alkali fusion will not proceed smoothly at any practical temperature.

(3) In 2-naphthol and 2-naphthylamine sulphonic acids, the order is 4-5-8-7-3-1- and the most resistant of all is -6-."

Method (g) Bucherer formulated two rules which should be followed.

(1) The reaction does not take place if a sulphonic acid group is ortho or meta to a -l-'OH' or 'NH₂' group.

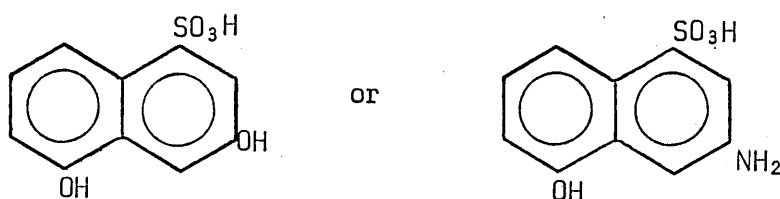
Thus in :-



only the 'OH' group in the 6 or 7 position will react.

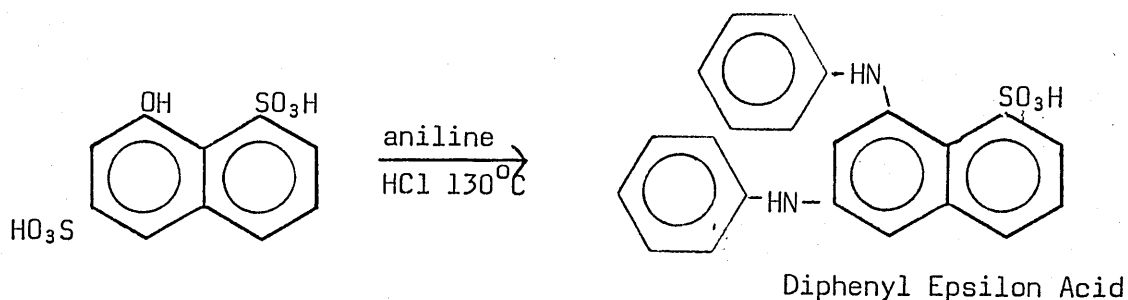
(2) The reaction does not take place if a sulphonic acid group is meta to a -2- 'OH' or 'NH₂' group.

Thus in :-



only the 'OH' group in the -5- position will react.

Method (h) This was the method of a patent by Kalle⁴ which has been investigated in the laboratory, but after many repeats and variations not the slightest trace of an amino compound has been detected. However, if the ammonia was replaced by aniline and the ammonium chloride by hydrochloric acid, a high yield of the diphenylamino compound was formed.

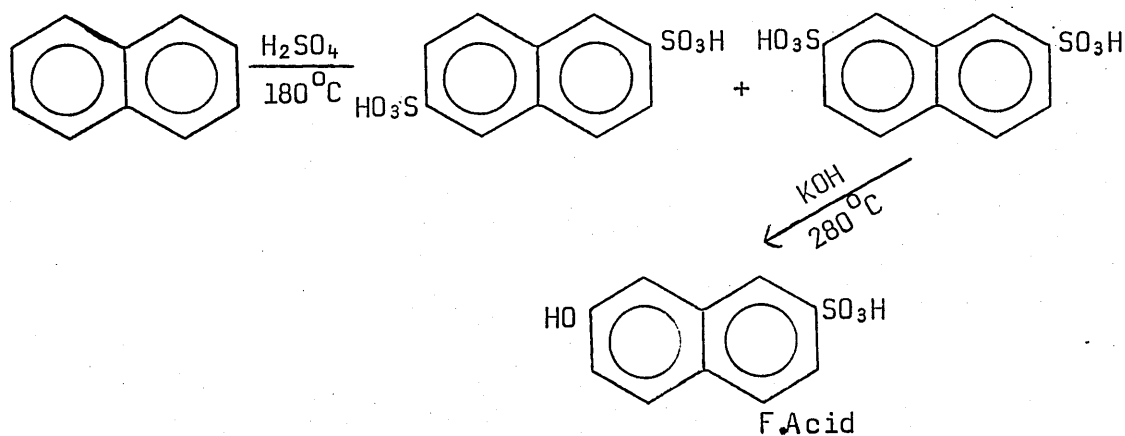


The above are given as methods of synthesis of Amino Hydroxy Naphthalene Sulphonic Acids, but it must be emphasised that

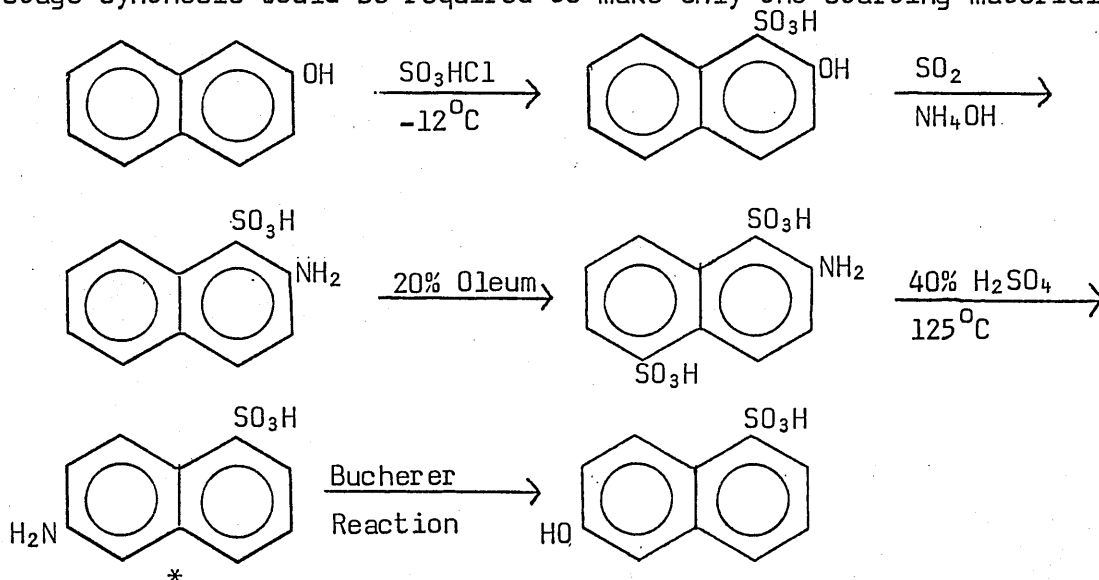
these methods only give the critical stage of the synthesis. If the preparation of the compound was the main objective, then provided the starting material was available, these methods would be satisfactory.

However, the main emphasis of this report is to review methods from a commercial angle, and therefore the synthesis must be considered from a well established product such as 2-hydroxy-naphthalene or naphthalene itself.

To illustrate this further, Method (b) required a hydroxy-naphthalene-sulphonic acid; 6-hydroxy-naphthalene-2-sulphonic acid (Schaeffer Acid) was a commercial product, so this was acceptable as a starting material. If however 7-hydroxy-naphthalene-2-sulphonic acid (F.Acid) was required, the synthesis would have to be considered from naphthalene, as follows :-



If, 6-hydroxy-naphthalene-1-sulphonic acid was required then a five stage synthesis would be required to make only the starting material.

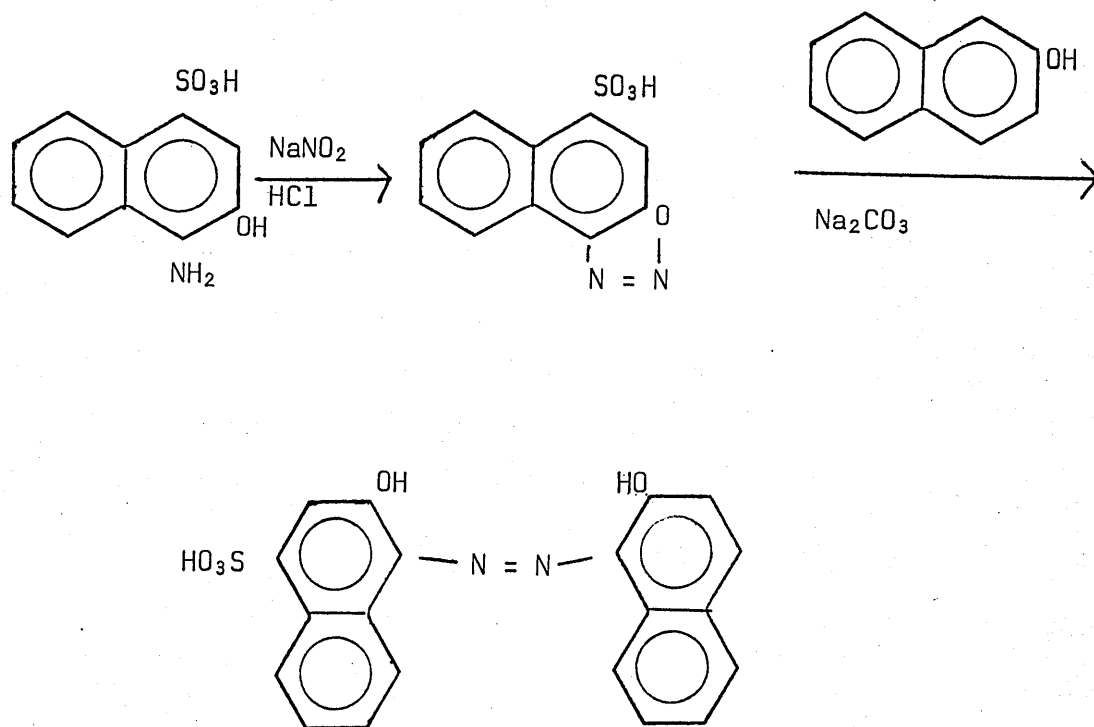


1.5 The Use of Amino Hydroxy Naphthalene Sulphonic Acids as Components in Dyestuff Preparation

Azo colours are pre-eminent, accounting for over 50% of all manufactured dyestuffs and pigments. This is because they are easily prepared from readily available intermediates of which Amino Hydroxy Naphthalene Sulphonic Acids are an essential part. They are characterised by the presence of Azo ($-N=N-$) groups (usually 1 or 2) in the molecule and are invariably prepared by diazotising a primary aromatic amine with nitrous acid in mineral acid solution and coupling the resultant diazonium salt with a phenol, arylamine or keto-enolic compound. The Amino Hydroxy Naphthalene Sulphonic Acids are very special in this respect since they can be used either as the diazo component, or the coupling component. These features are shown in the four examples below.

1.5.1 Use as a diazo Component

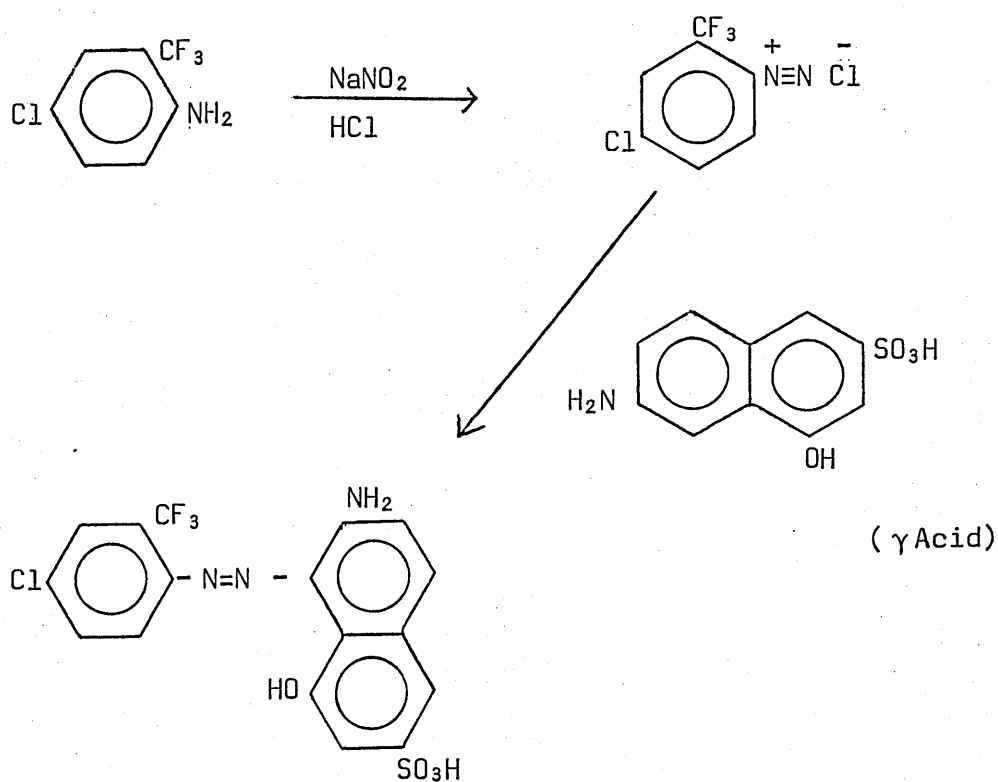
The amino-hydroxy-naphthalene-sulphonic acid was charged into water, ice, and hydrochloric acid; at 0-5°C a solution of sodium nitrite added until a permanent blue colour was obtained on Starch Iodide Test Paper. The diazo solution (or slurry) was then run into the coupling component in the presence of excess sodium carbonate.



(Black Dyestuff)

1.5.2 Use as a Coupling Component under Acid Conditions

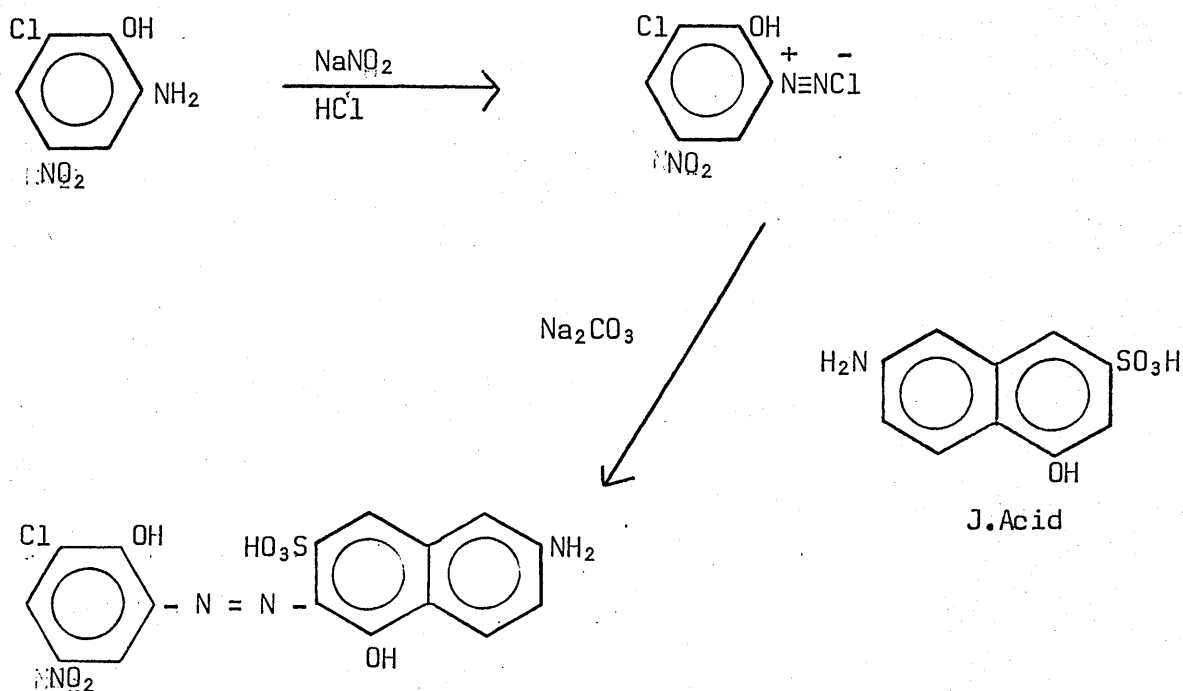
The amine was diazotised as in 1.5.1 and then a slurry of the amino-hydroxy-naphthalene-sulphonic acid was run into the diazo solution. The coupling was slow and sometimes required stirring for 24 hours to complete the reaction.



(Red Dyestuff)

1.5.3 Use as a Coupling Component under Alkaline Conditions

The amine was diazotised as in 1.5.1, and then run into a solution of the sodium salt of the amino-hydroxy-naphthalene-sulphonic acid. A pH of 7.5-9.0 was maintained throughout the addition.

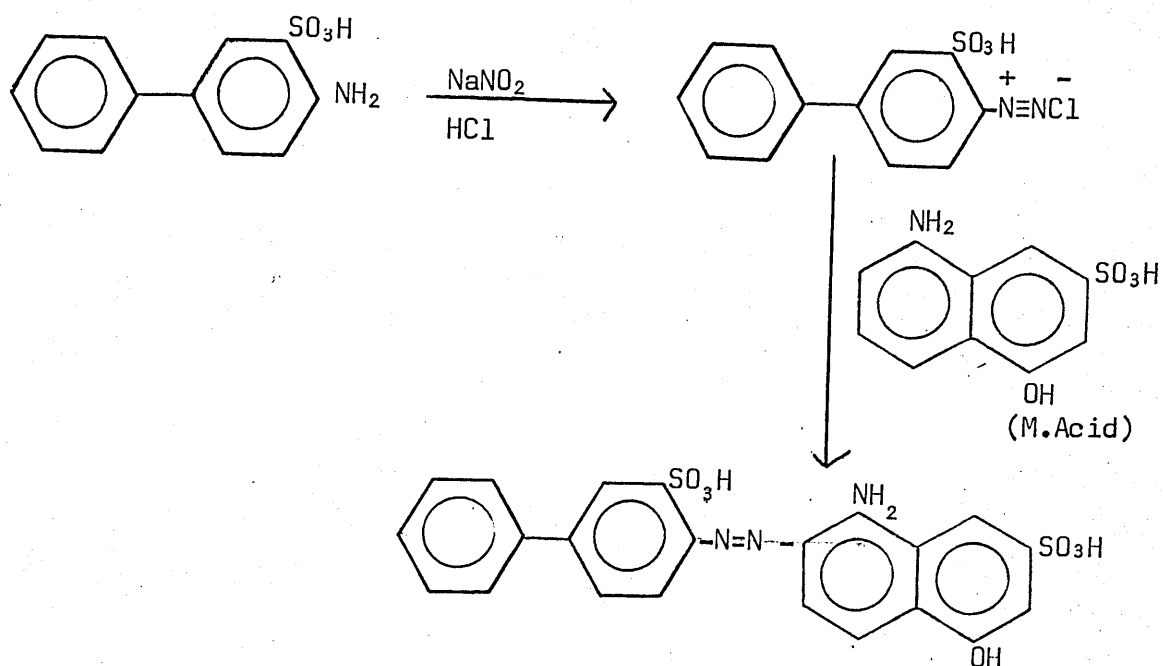


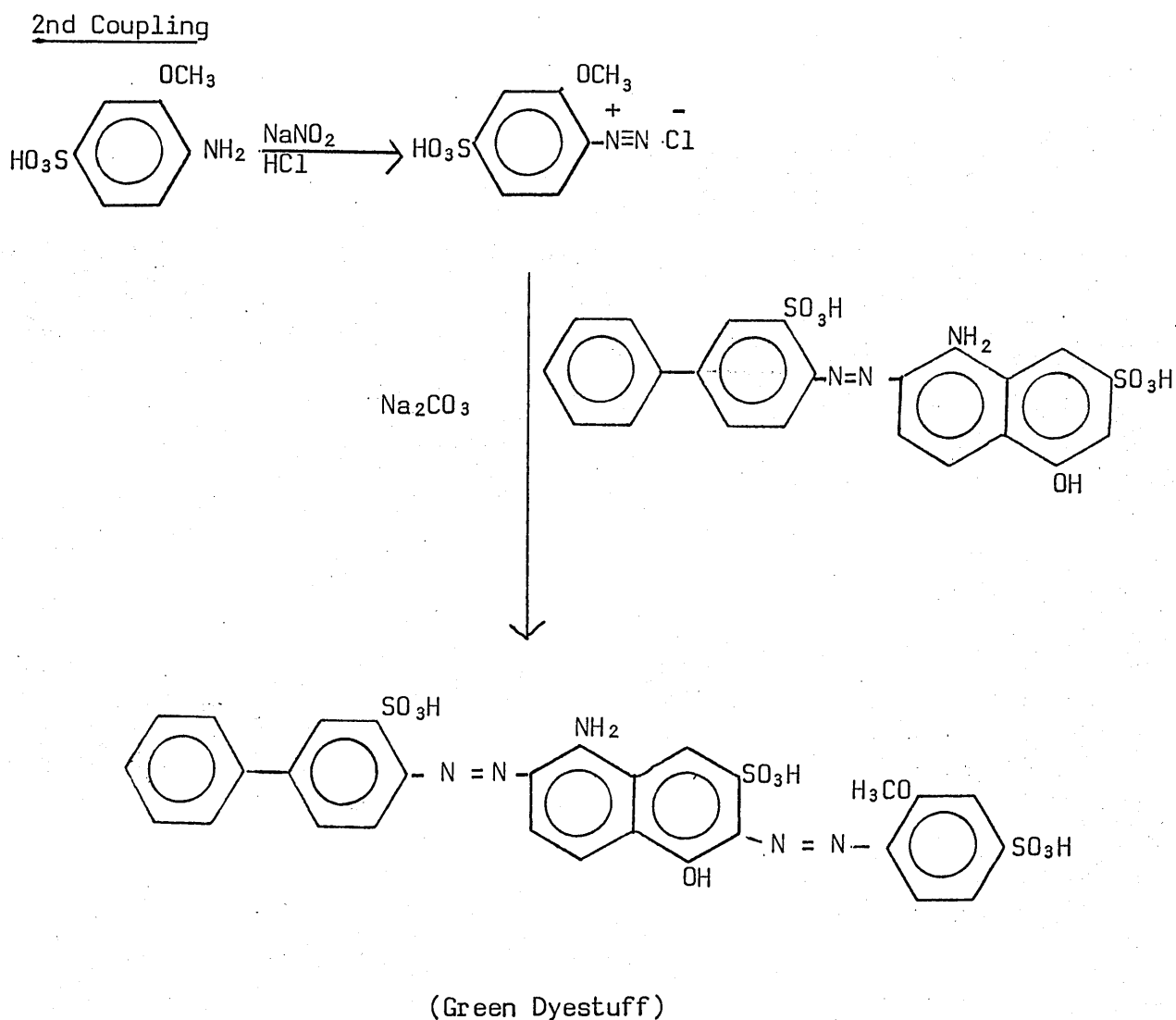
(Black Dyestuff)

1.5.4 Use as a Middle Coupling Component

In this example, two couplings were made onto the amino-hydroxy-naphthalene-sulphonic-acid, one under acid conditions and one under alkaline conditions. The reactions must always be carried out in that order.

1st Coupling





1.5.5 Comments on the Methods of Preparation of Azo Dyestuffs

The procedure for carrying out these preparations is straight-forward provided that it is only a laboratory experiment to prepare the desired compound. If however, the compound is being prepared as an example of a commercial dyestuff which in a single batch may produce quantities of Standard colour from one tonne to 88 tonnes, then very strict and accurate procedures would have to be followed since a slight variation in pH, concentration

temperature, rate of addition etc. could and would affect shade, solubility, light fastness or physical form. To ensure not only a satisfactory product but a repeatable one, an experienced operator would be required.

The following example is given which describes with full details the preparation of a commercial dyestuff to illustrate this strict procedure.

Diazotisation

The amine (0.1mol) was added to water (40ml) ice (25g) and HCl 36% (85g, .84mol) and stirred for 6 hours at 0-5°C. (Note: external cooling would be required in the laboratory) sodium nitrite solution 40% (19ml, .11mol) was added at 0-5°C and then stirred 2 hours and then diluted to 2000ml with ice (600g) and water. The excess sodium nitrite was removed by the addition of sulphamic acid, and sodium bicarbonate (39g, .465mol) added evenly over 20 minutes.

Preparation of Coupling Component

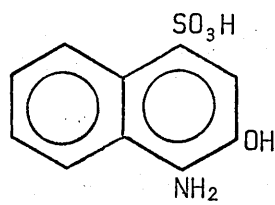
Gamma Acid (25g, .105mol) was added to a mixture of water (200ml), caustic soda 32% (11ml, .119mol) and stirred for 10 minutes. Before coupling, sodium carbonate (2g, .019mol) was added with ice to cool to 2°C. HCl 36% (12ml, .016mol) was then added to precipitate the Gamma Acid.

Coupling

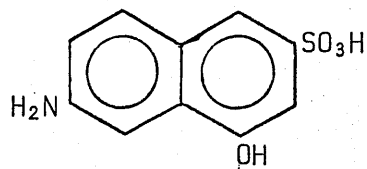
The Gamma Acid slurry was run into the diazotisation mixture at 0-2°C over 5 minutes and stirred for 15 hours at 0-10°C. salt (480g) was added to precipitate the dyestuff, and after 1 hour caustic soda (32%) was added such that the mass was not acid to Congo Red Test Paper (pH 3.0 approx.), sodium carbonate (6g, .56mol) was then added and after 3 hours the slurry was heated to 50°C to change the physical form, before filtering off, washing with neutral brine (200ml) and finally drying at 40-45°C. (62.7g, 89%).

1.6 Synthesis of the Five Manufactured Compounds (The Big Five)

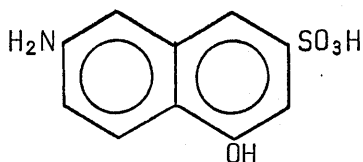
These compounds have the following constitutions:-



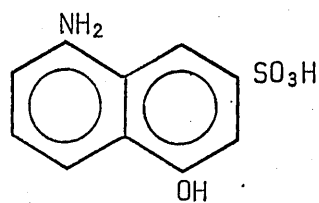
1:2:4 Acid



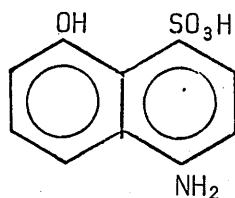
γ Acid



J.Acid



M.Acid



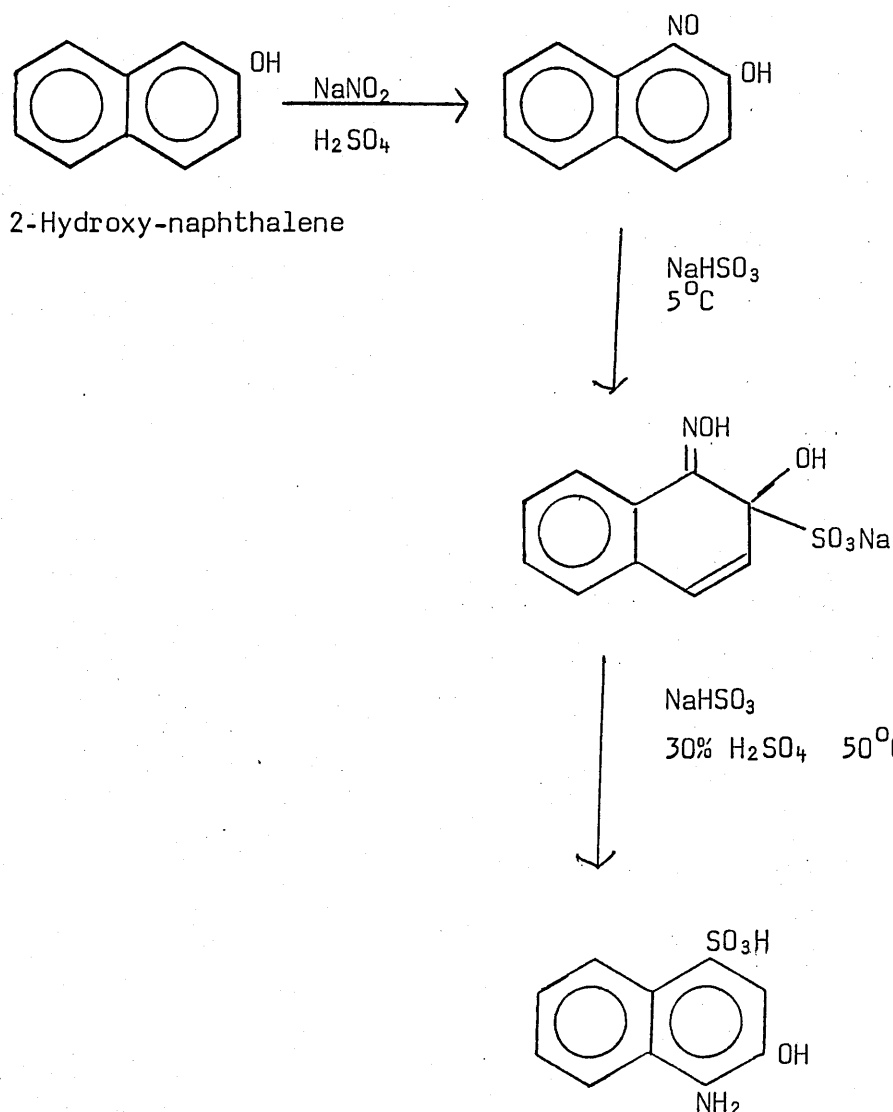
S.Acid

Before describing the synthesis of these isomers, it is interesting to note the relationship between them.

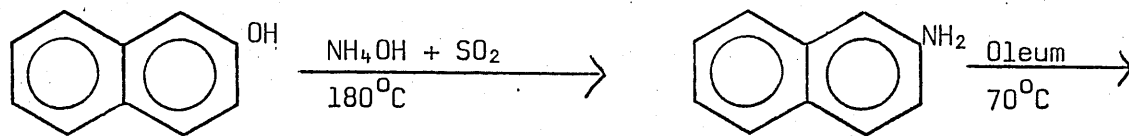
- (1) 1:2:4 Acid, γ , J, and M Acids all have the meta hydroxy-sulphonic acid configuration.
- (2) γ , J, and M Acids are the 6, 7 and 8 amino isomers of 4-hydroxy-naphthalene-2-sulphonic acid.
- (3) 1:2:4 Acid, γ , and J Acids each require 2-hydroxy-naphthalene as the base material for preparation.

The relationships given in (1) and (2) might suggest a similar method of preparation but this would be completely wrong. (3) does give an indication of the products which are most readily available, because the base material is manufactured in such large quantities and therefore relatively cheap.

1.6.1 Synthesis of 1.2.4 Acid

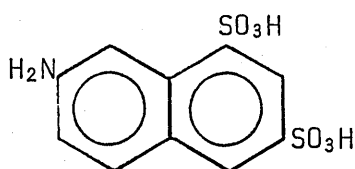


1.6.2 Synthesis of γ and J Acids

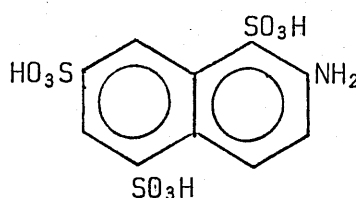


2-Hydroxy-naphthalene

2-Amino-naphthalene

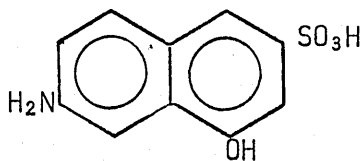
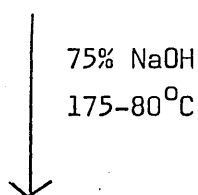


Amido G. Acid

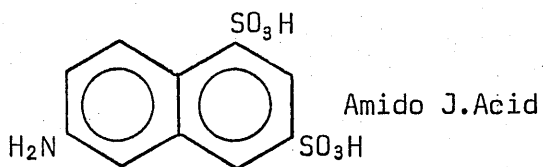
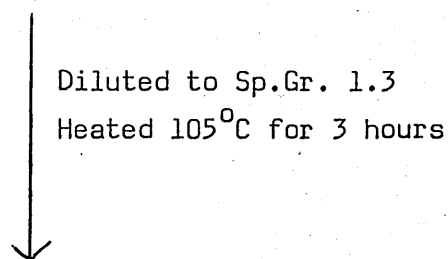


2-Amino-naphthalene-1,5,7-trisulphonic acid

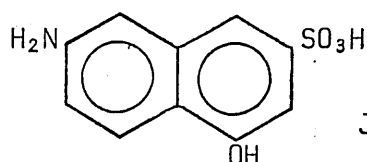
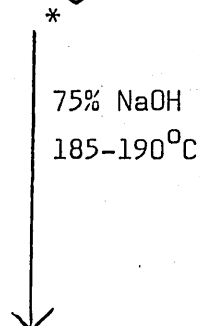
at this stage the Amido G Acid is filtered off, being insoluble in the acid liquors.



γ Acid

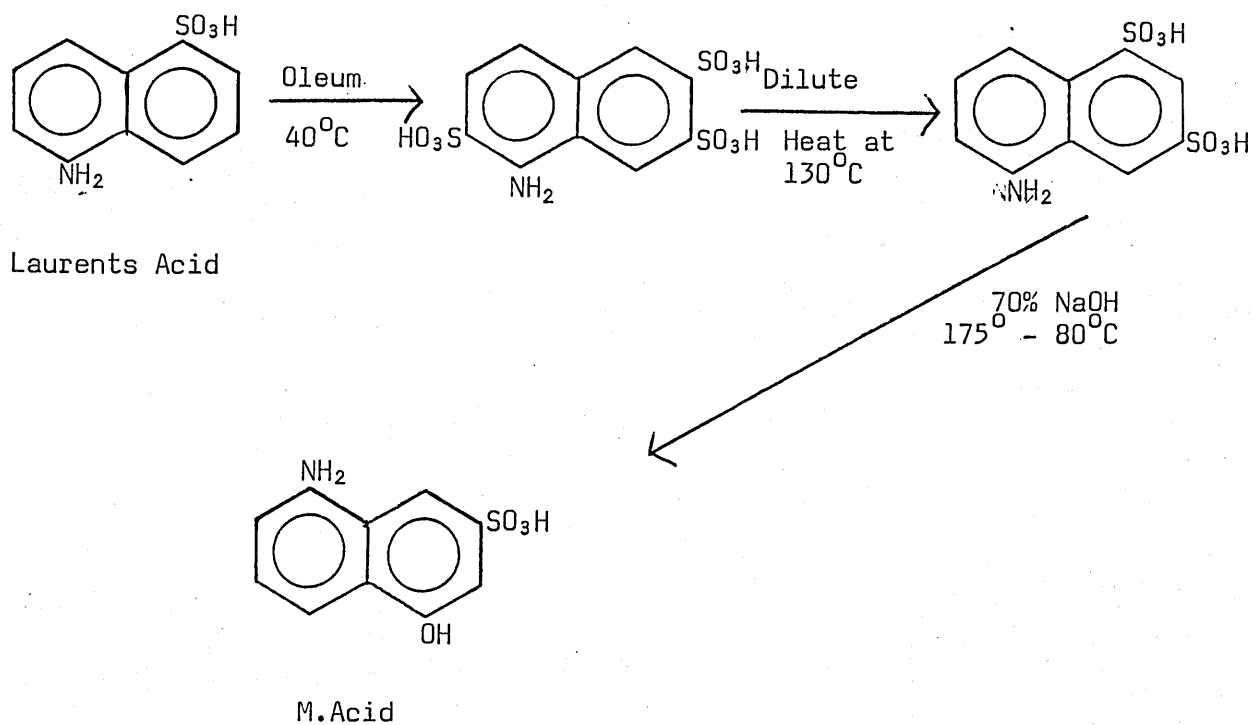


Amido J. Acid

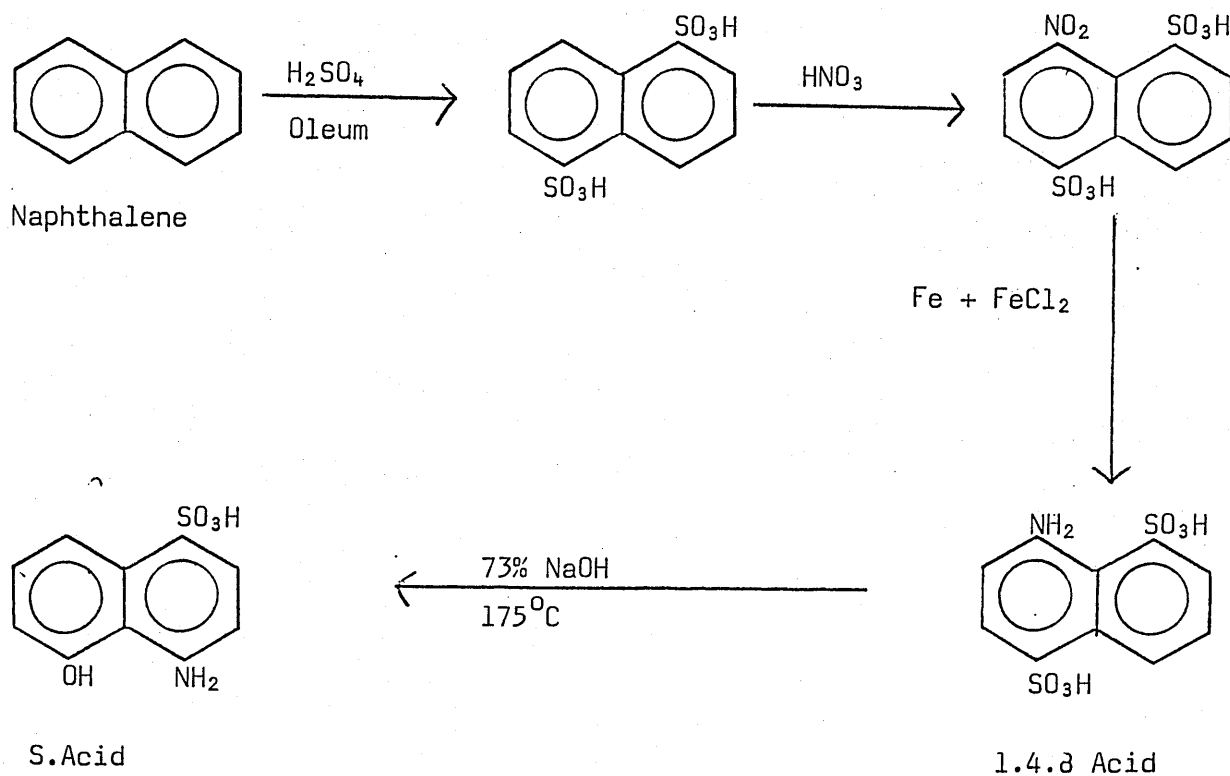


J. Acid

1.6.3 Synthesis of M.Acid



1.6.4 Synthesis of S.Acid



2.0 Tables of all the Reported Amino Hydroxy Naphthalene Sulphonic Acids

Tables 1 and 2 list all the amino hydroxy naphthalene-sulphonic acids recorded by Thorpe¹ and Donaldson² together with those reported in the period under review irrespective of whether or not a method of preparation has been given.

Table 1 lists those isomers with a -1-sulphonic acid group, and Table 2 those with a -2-sulphonic acid group.

By analysing these Tables, it can be seen that Thorpe recorded 48 isomers including 2 not recorded by Donaldson and Donaldson 49 which included 3 not recorded by Thorpe. Thus in 1953 a total of 51 isomers were known together with methods for their preparation.

In the period under review 48 isomers were reported in Chemical Abstracts, 40 of these were previously recorded by Thorpe or Donaldson; 8 were unknown isomers and these are discussed in Section 4.

In Tables 1 and 2

For the column headed 'a' read Thorpe

For the column headed 'b' read Donaldson

TABLE 1 Summary of Compounds Recorded in the Literature

Group Position NH ₂ -OH SO ₃ H			a b		Chemical Abstracts Index								
					Collected Volumes No.						Single Volume No.		
					5	6	7	8	9	10	96	97	
2	3	1											
2	4	1											
2	5	1	X	X	X								
2	6	1											
2	7	1					X						
2	8	1											
3	2	1											
3	4	1	X	X			X	X	X	X			
3	5	1			X			X					
3	6	1											
3	7	1	X	X		X							
3	8	1					X						
4	2	1	X	X			X						
4	3	1	X	X	X	X	X	X	X	X	X	X	X
4	5	1	X	X	X	X	X	X	X	X		X	
4	6	1	X	X	X			X					
4	7	1	X	X	X			X					
4	8	1	X	X	X								
5	2	1											
5	3	1	X	X	X								
5	4	1	X	X	X	X	X						
5	6	1	X	X	X		X	X		X			
5	7	1											
5	8	1	X	X									

TABLE 1 Continued

Group Position NH ₂ -OH-SO ₃ H			a b		Chemical Abstracts Index								
					Collected Volumes No.						Single Volume No.		
					5	6	7	8	9	10	96	97	
6	2	1											
6	3	1			X							X	X
6	4	1	X	X	X			X	X	X			
6	5	1	X	X	X		X	X	X				
6	7	1											
6	8	1											
7	2	1											
7	3	1	X	X	X	X	X			X			
7	4	1	X	X					X	X			
7	5	1	X	X									
7	6	1											
7	8	1	X	X	X		X						
8	2	1											
8	3	1	X	X	X								
8	4	1	X	X	X								
8	5	1		X									
8	6	1											
8	7	1	X	X			X						

TABLE 2 Summary of Compounds Recorded in the Literature

Group Position NH ₂ -OH-SO ₃ H	a b		Chemical Abstract Index									
			Collected Volumes No.							Single Volume No.		
	5	6	7	8	9	10	96	97				
1 3 2												
1 4 2	X	X		X								
1 5 2	X	X	X									
1 6 2												
1 7 2												
1 8 2	X	X										
3 1 2												
3 4 2	X	X			X							
3 5 2												
3 6 2	X											
3 7 2			X									
3 8 2												
4 1 2	X	X										
4 3 2				X					X			
4 5 2	X	X		X	X	X	X					
4 6 2	X	X	X	X	X							
4 7 2	X	X	X			X						
4 8 2								X				
5 1 2	X	X	X	X	X			X	X			
5 3 2												
5 4 2	X	X	X	X	X			X	X		X	
5 6 2	X	X	X	X	X	X		X		X	X	
5 7 2	X	X										
5 8 2	X	X										

TABLE 2 Continued

Group Position NH ₂ -OH-SO ₃ H	a b		Chemical Abstract Index							
			Collected Volumes No.						Single Volume No.	
			5	6	7	8	9	10	96	97
6 1 2	X			X	X					
6 3 2		X				X				
6 4 2	X	X	X	X	X	X	X	X	X	X
6 5 2		X						X		
6 7 2	X	X		X	X		X	X		
6 8 2	X	X								
7 1 2	X	X	X							
7 3 2										
7 4 2	X	X	X	X	X	X	X	X	X	X
7 5 2	X	X	X							
7 6 2										
7 8 2	X	X								
8 1 2	X	X								
8 3 2										
8 4 2	X	X	X	X	X	X	X	X		X
8 5 2	X	X			X					
8 6 2				X						
8 7 2	X	X				X	X			

3.0 Information on the Preparation of Isomers Recorded up to 1953

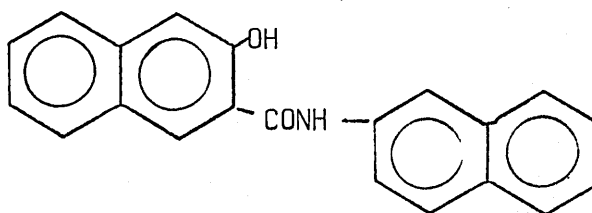
This section details the methods of preparation reported in the literature in the review period 1953 - 1982. Before the information can be clearly understood or seen in its true perspective, it is necessary to describe the external factors which were responsible to a great extent for an almost complete change of direction of the research and manufacturing programme.

The three major chemical companies of the world, I.G. (Germany, I.C.I. (Great Britain) and DuPont (America) were well informed of each other's work. Thus the information recorded in the post war intelligence reports B.I.O.S.⁵ and F.I.A.T.⁶, which are the only publically available documents, give a clear outline of the research activities of all the companies.

The intensity of research and potential production of the non-manufactured isomers was of paramount importance to the financial success of the companies, and to ensure they were equipped to produce these new products and any new intermediates, large investment plans were made to meet the anticipated huge demand.

Therefore, in anticipation of the boom, one company built three new manufacturing plants for naphthalene compounds. These were a 2-hydroxy-naphthalene (β Naphthol) plant, to produce 150,000 Kg per week; a general naphthalene intermediates plant and a 2-amino-naphthalene (β naphthylamine) plant. This latter plant

was large enough to produce sufficient material for all the J and γ acids and also for the very important Azoic Dyestuff component 'Naphthol' BN which gave Turkey Red shades with the appropriate diazo compound

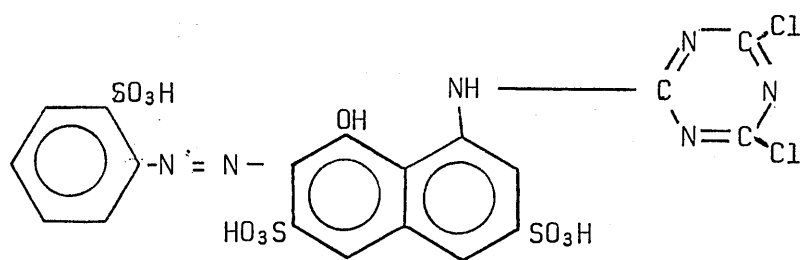


Naphthol BN

and for any Azo direct cotton dyestuff.

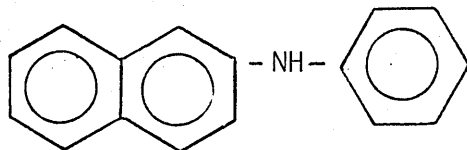
Some of the events which caused the change of direction are given below; they are in no particular order of importance or of time sequence, with the exception of the first one which was of major importance.

- (a) The cessation of manufacture in the period 1950 - 1955 of 2-amino-naphthalene (β naphthylamine) because of its carcinogenic effects on the work force. This meant that new processes were required for J and γ acids, and those are described in Section 5.
- (b) The discovery of Reactive Dyestuffs by W. E. Stephen⁷ (I.C.I.) and their manufacture in 1956 under the trade name of "Procion Dyestuffs." The first examples were monoazo dyestuffs which had a free amino group that had been reacted with cyanuric chloride to give the reactive dyestuff. Procion Red M5B is an example.



These dyestuffs could be used in cold water and gave fast shades, superior to those obtained from traditional dyestuffs.

- (c) Elimination of the Azoic range of dyestuffs all of which consumed 2-hydroxy-naphthalene (β Naphthol) thus reducing the demand for this intermediate.
- (d) Elimination of 2-Phenylamino-naphthalene (Phenyl β naphthylamine)



from the manufacturing range because of its 2-amino-naphthalene content. Much of this was manufactured from fore and end runnings of the 2-hydroxy-naphthalene distillation which were unsuitable for other uses. The product was an anti-oxidant for rubber.

- (e) The cleaning up of the environment i.e. air pollution, discharge to sewers and rivers, safety in manufacturing plants etc. One company discharged acid liquors direct

into the river because the river bed was limestone.

Off gases such as nitrous fumes from a nitration or ammonia from an amination had to be scrubbed and any waste material such as gypsum could not be tipped indiscriminately.

- (f) The up-grading of the status of the plant operators in the larger companies (i.e. I.C.I.) from chemical labourers to process operators, which together with (e) above, resulted in a change of emphasis on costing from materials to expenses.

When material costs were predominant it was essential to get the maximum yield, however when expenses had become predominant, throughput became important. Thus if the yield from a reaction was 70% after 5 hours and 87% after 15 hours then the longer reaction time was used when materials were important whereas the shorter reaction time was used when expenses were predominant.

- (g) The cost of building replacement plants with all the refinements required by modern standards.

This situation can be illustrated by the following example. A reaction involving Methanol as solvent was to be carried out in a standard glass lined pan at 90°C under about 14 p.s.i. pressure. The cost of refinements to the unit would under regulations at the start of this review period have been about £20,000 mainly for an elaborate gland for the agitator.

To conform with modern regulations at the same costing basis, the cost of the refinement of the unit was about £800,000.

- (h) The introduction of man made fibres such as Nylon, Polyester and Terylene which cannot be dyed with the traditional dyestuffs.

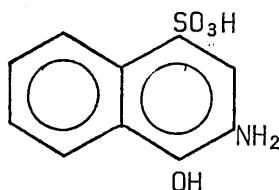
There were without doubt other factors but these are clearly the most important ones.

With this in mind, it is therefore not surprising, that on searching the literature, of the 51 compounds known in 1953 only 40 were found in the period under review, and, omitting the 'Big Five' only 17 methods of preparation were recorded. Most of these methods were of academic interest only. Of the major chemical manufacturing companies, only Bayer A.G. (Germany) and Ciba-Geigy (Switzerland) appeared to be interested in the research and manufacture of this type of compound.

Finally, it must be emphasised that the new methods which are recorded below are only the final stages of the synthesis. Thus these routes, like those given in Section 1.4, still suffer from the problems associated with the base materials. This alone may have been the

crucial factor for the lack of interest in producing further isomers or even continuing to produce those already made.

The following compounds were recorded with their methods of preparation.



The two methods of preparation of Isomer 341 from 4-hydroxy-naphthalene-1-sulphonic acid (N.W.Acid) had been known for 90 years. These were (a) nitrosation and reduction and (b) coupling and splitting of the diazo compound.

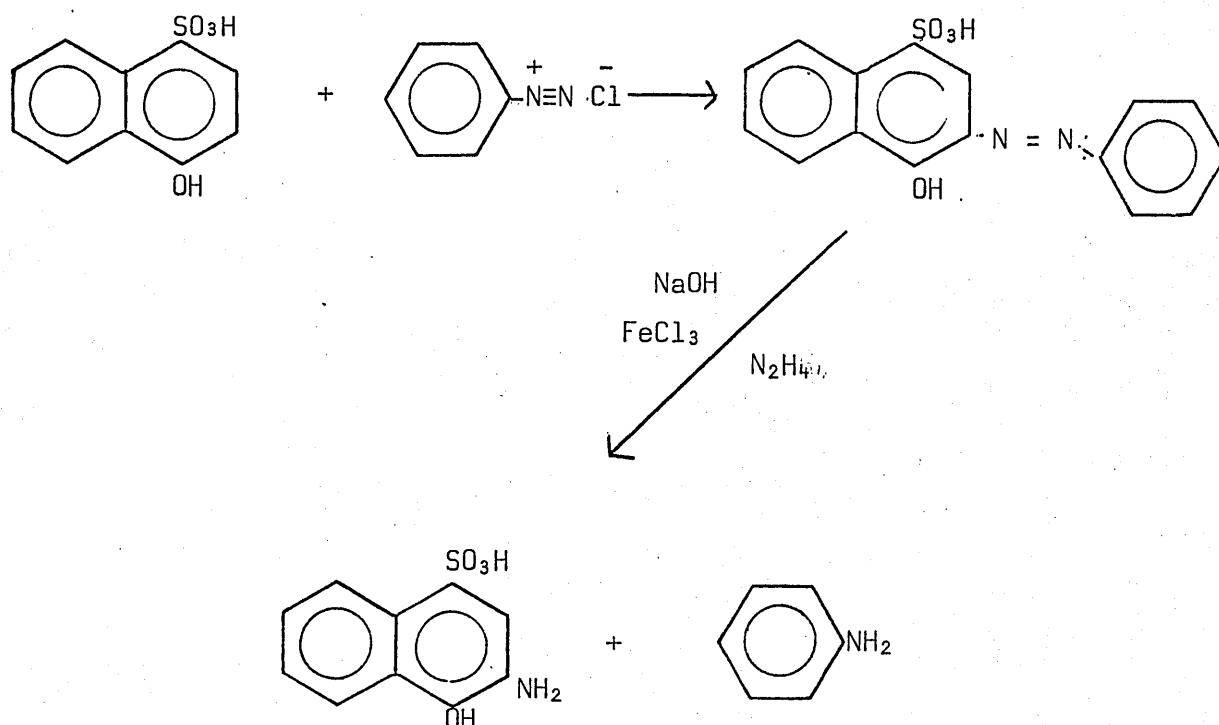
In 1976 a Russian Patent⁸ described the nitrosation route, but added little to the information already known. The patent did however describe the diazotisation of the Isomer 341 using special dispersing agents.

Also in 1976 a Japanese Patent⁹ described the other route and gave details of a new reduction procedure for the azo compound.

"Hydrazine hydrate 10% (320g) was heated with a mixture of the azo compound aniline \longrightarrow N.W.Acid (328g), caustic soda (60g) ferric chloride (8g) in water for 2 hours at 60-70°C to give 85% yield of Isomer 341."

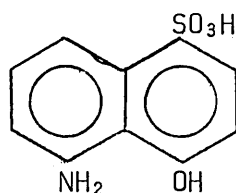
This new route would be very acceptable commercially since the alternative routes left much to be desired. Hydrazine hydrate has become much more readily available in recent years at a much reduced cost and therefore Isomer 341 could probably be manufactured by this process at an economic price should it be

commercially required.



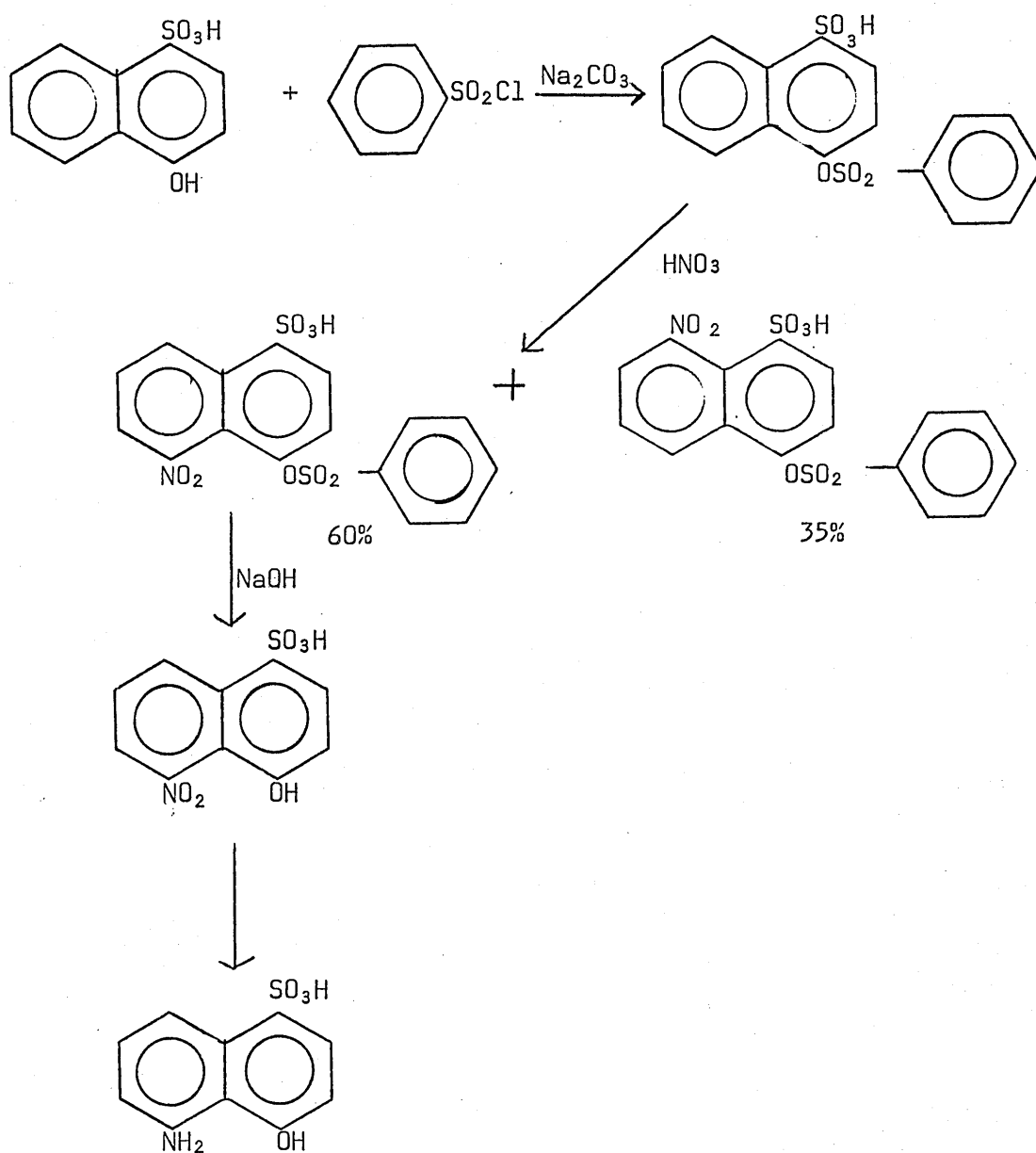
NOTE: Aniline \rightarrow N.W. Acid is the literature abbreviation for describing the dyestuff formed of coupling diazotised aniline onto N.W. Acid.

3.2 Isomer 541

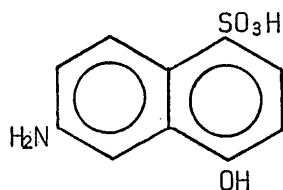


The three references to this isomer gave no method of preparation, but a reference was found in 'AKO' reports.¹⁰

This gave the method of preparation, without details, as follows:-

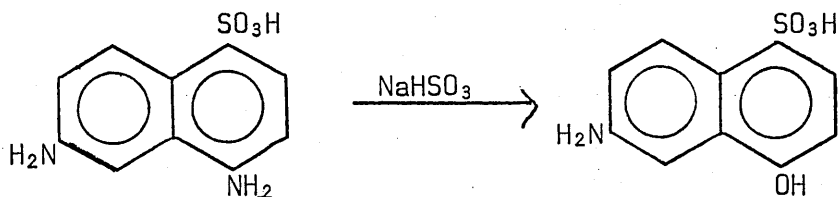


Isomer 541

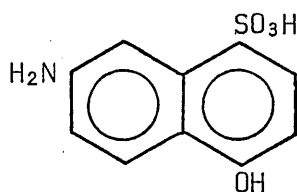


The method of preparation, patented by Bayer A.G.¹¹ was reported as a manufacturing process. The details are as follows:-

"1, 7-Diamino-naphthalene-4-sulphonic acid (0.1mol) was charged into sodium bisulphite 38% (400ml) at 95°C and held at that temperature for 5 hours; it dissolved after a short time to give a yellow colour. hydrochloric acid was then added and air blown to remove SO₂ maintaining acidity to Congo Red Test Paper. Caustic soda 40% (60ml) was added until alkaline and heated at 80°C for half an hour, before making acid again and then stirred until cold. Yield was 80%."

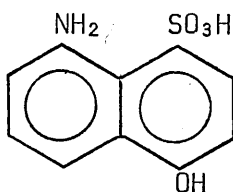


Isomer 641



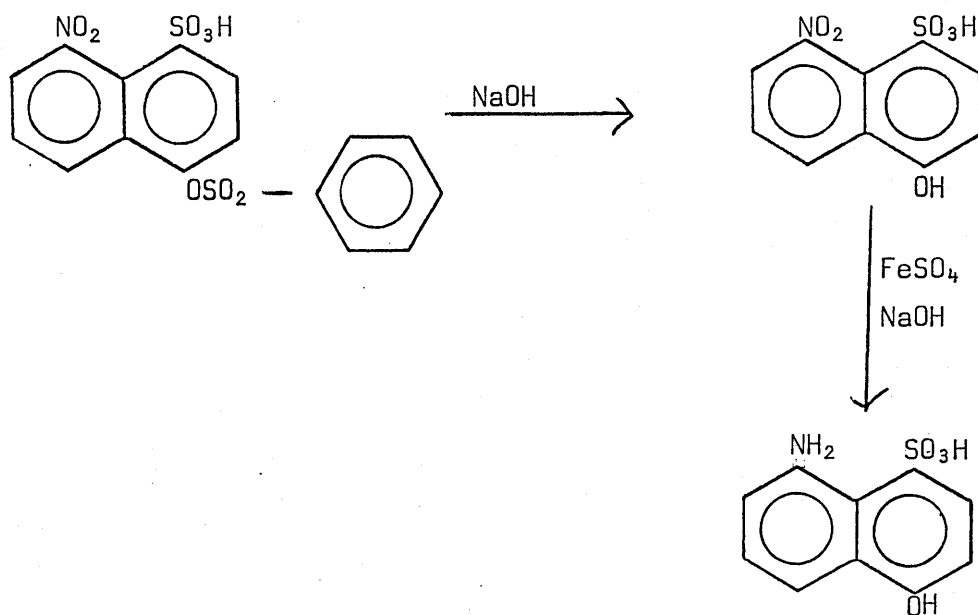
No direct method for this Isomer was found, but a Ciba-Geigy Patent¹² listed it in a general patent headed "Semi-Continuous Manufacture of Aromatic Amines", this involved the reduction of nitro compounds by the standard iron-ironsalt method at 50-110°C. The method of preparing the required base material 7-nitro-4-hydroxy-naphthalene-1-sulphonic acid was not disclosed.

3.5 Isomer 841



The base material for this isomer was obtained from the filtrates of Isomer 541 (Section 3.2) by salting with salt.¹⁰ This was then hydrolysed with caustic soda to give 8-nitro-4-hydroxy-naphthalene-1-sulphonic acid. It was stated that the reduction of this was very difficult because it readily desulphonated. The best reagent to this reduction was ferrous sulphate in alkaline medium.

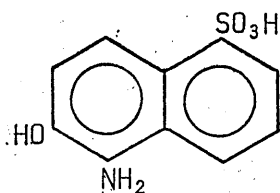
A very popular reducing agent for intermediates of this type is $\text{Na}_2\text{S}_4 \cdot 2$ made by the addition of sulphur to sodium sulphide crystals and heating to dissolution. The reasons why this exact compound works so well are not understood but it has been used by the Author on many occasions with great success.



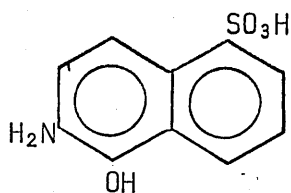
Isomer 841

3.6 Isomers 561, 651, 562, and 872 - All made by the same method

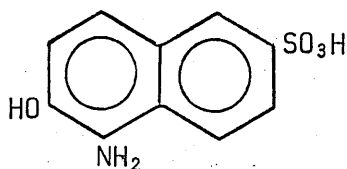
The following four isomers



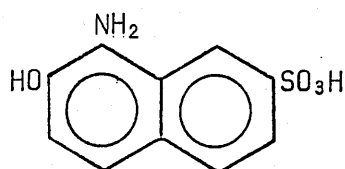
561



651



562



872

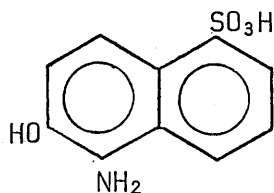
have previously been made from their respective hydroxy-naphthalene-sulphonic acids, that is :

- 561 from 6-hydroxy-naphthalene-1-sulphonic acid
- 651 from 5-hydroxy-naphthalene-1-sulphonic acid (Oxy-L-Acid)
- 562 from 6-hydroxy-naphthalene-2-sulphonic acid (Schaeffer Acid)
- 872 from 7-hydroxy-naphthalene-2-sulphonic acid (F.Acid)

This involves coupling with a diazotised amine and reducing, or by nitrosating and reducing. Both methods were quite satisfactory but in the coupling method the choice of the amine is important since it has to be removed completely after reduction so that the isomer can be isolated pure.

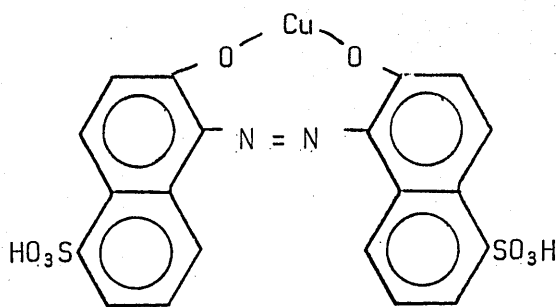
This problem was eliminated by a new method patented by Bayer¹³ in which specific amino naphthalene sulphonic acids were

diazotised and coupled with the relevant hydroxy naphthalene sulphonic acid. The unsymmetrical dyestuff was then oxidised and converted to the symmetrical copper complex, which gave on reduction only the required isomers as shown in Sections 3.7-3.10.

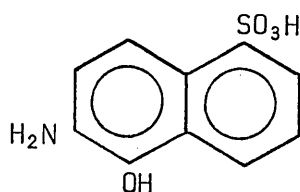


The Bayer patent¹³ described the preparation as follows:-

"5-Amino-naphthalene-1-sulphonic acid (Laurents Acid) 22.3g, was diazotised by the known method, and coupled in alkaline medium with 6-hydroxy-naphthalene-1-sulphonic acid 24g, at a total volume of 1000 ml. To this was added copper sulphate crystals (28g), sodium acetate (35g), and acetic acid (15ml), then hydrogen peroxide 3% (300ml), added dropwise over 2 hours. By the addition of potassium chloride the symmetrical dyestuff with the following constitution was isolated.

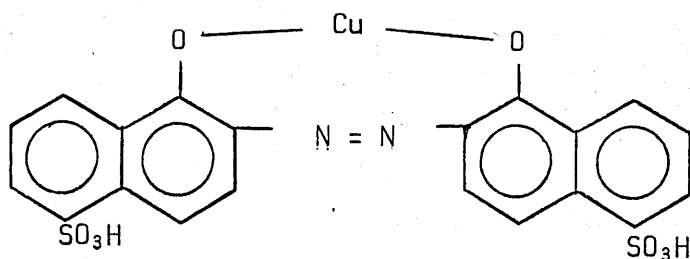


The dyestuff was dissolved in water at 70°C by the addition of caustic soda 40% (20ml), and reduced by the addition of sodium dithionate. After 15-20 minutes the solution was treated with activated charcoal, and acidified to precipitate the isomer, which after cooling was filtered off to give 37.2g (78% Theory)".



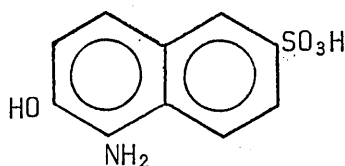
The Bayer Patent¹³ described the preparation as follows:-

"6-Amino-naphthalene-1-sulphonic acid 22.3g, was diazotised by the known method, and coupled in alkaline medium with 5-hydroxy-naphthalene-1-sulphonic acid (Oxy-L Acid) (24g), at a total volume of 1000ml. To this was added copper sulphate crystals (28g), sodium acetate (35g), acetic acid (15ml), followed during 2 hours by hydrogen-peroxide 3% (300ml), at 50°C dropwise when a compound of the following constitution was obtained.



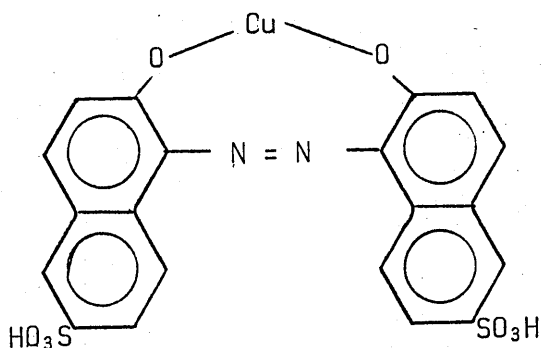
The dyestuff was isolated by acidifying with hydrochloric acid and salting with potassium chloride.

The dyestuff was dissolved in 400ml water and caustic soda 40% (20ml) and reduced with sodium dithionate (53g). After 15-20 minutes the solution was treated with activated charcoal and acidified at room temperature. The isomer yield was 25 g (52% Theory)."



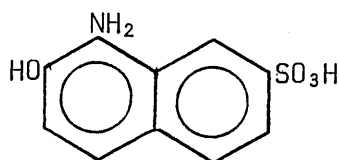
The Bayer Patent¹³ described the preparation as follows:-

"5-Amino-naphthalene-2-sulphonic acid (22.3g), was diazotised by the known method, and coupled in alkaline medium with 6-hydroxy-naphthalene-2-sulphonic acid (Schaeffer acid) (24g), at a total volume of 1000 ml. To that was added copper sulphate crystals (28g), sodium acetate (35g) and acetic acid (15 ml), followed during 2 hours by hydrogen peroxide solution 3%(300ml), dropwise at room temperature whereby was obtained the copper complex with the following constitution.



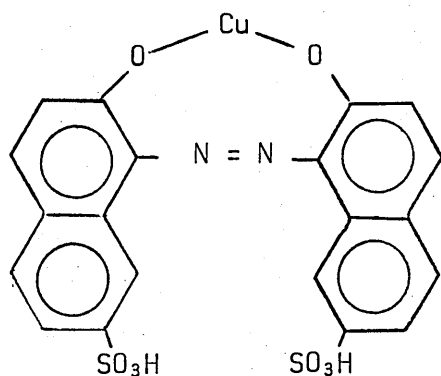
The dyestuff was isolated by acidification and salting with potassium chloride.

The dyestuff was dissolved in water (400ml), and caustic soda 40% (20ml) and reduced with sodium dithionate (53g). After 15-20 minutes the solution was treated with activated charcoal, acidified and cooled to room temperature. The isomer yield was 27g, (56% Theory)."



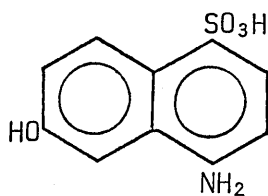
The Bayer patent¹³ described the preparation as follows:-

"8-Amino-naphthalene-2-sulphonic acid (1,7 Cleve Acid) (22.3g), was diazotised in the known manner and coupled in alkaline medium with 7-hydroxy-naphthalene-2-sulphonic acid (F.Acid)(24g), at a total volume of 1000ml. When the coupling was complete the dyestuff was isolated, and dissolved in water (500ml), at 70°C. To that was added copper sulphate crystals (28g), sodium acetate (35g) and acetic acid (25ml), followed during 2 hours by hydrogen peroxide solution 3% (300ml) added drop-wise, whereby the copper complex of the following constitution was obtained:-



The complex was isolated by the addition of hydrochloric acid (Congo Red Reaction) and potassium chloride.

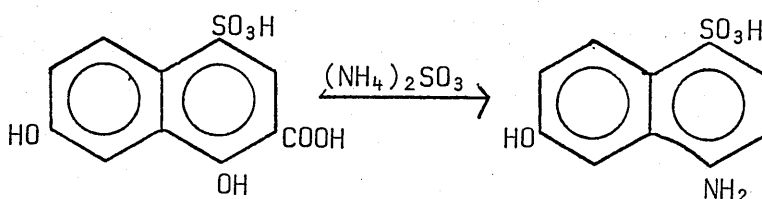
The complex was dissolved in water (400ml), at 75°C with caustic soda 40% (20ml), and reduced by the addition of sodium dithionate (53g). After 15-20 minutes the solution was treated with activated charcoal and the isomer precipitated with hydrochloric acid, cooled to room temperature and filtered off. The yield was 19.2g (40% Theory)."



Isomer 461 was considered a likely candidate for manufacture because when it, or its acyl and aryl derivatives were used as the coupling components - in alkaline couplings it gave green shades for wool and cotton and also blue-grey to grey shades when employed in chrome dyes. A lot of interest disappeared when it was found that the sulphonic acid group was not very stable and could migrate easily to the adjacent position giving the isomer 462, whose dyes were not as attractive.¹⁰

In 1968 Nickel and Suckful in a Bayer Patent¹⁴ described the preparation of the isomer as follows:-

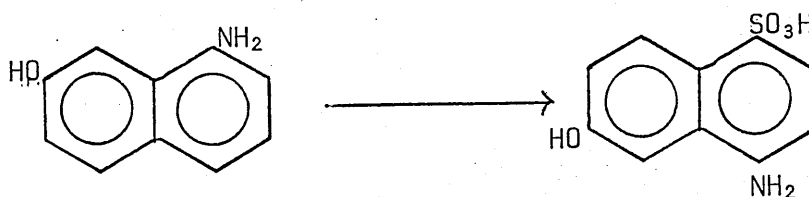
"1,7-Dioxy-2-carboxy-4-naphthalene-sulphonic acid (0.1mol) as a moist HCl or H₂SO₄ wet paste, was heated for 24 hours at 80°C with ammonium sulphite 3.6M (280ml). After acidifying with HCl (180ml) and removing the sulphur dioxide, it was made alkaline with caustic soda (100ml), stirred half an hour and filtered to give 80% yield."



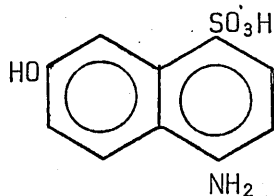
In the previous year (1967) a very long patent by Roe and Thiro¹⁵ revealed a completely new approach to synthesising naphthalene-sulphonic acids including Isomer 461.

The method of preparation was given as follows:-

"1-Amino-7-naphthol sodium salt (181 parts), MnO₂ (240 parts) sodium bisulphite 32% (1500 parts by vol.) were heated at 55°C until there was no trace of 1-amino-7-naphthol. The mass was then acidified and SO₂ removed, cooled and the 1-amino-7-naphthol-4-sulphonic acid (Isomer 461) filtered off. The product contained some -2,4-disulphonic acid."



Neither of the above methods were considered to be commercially viable. The method of heating 1-amino-7-naphthol with chloresulphonic acid in 1,2-dichlorobenzene with formic acid as catalyst¹⁶ which the Author had used many times was considered far superior especially if a dispersing agent was added to the reaction mass prior to the addition of the chloresulphonic acid.

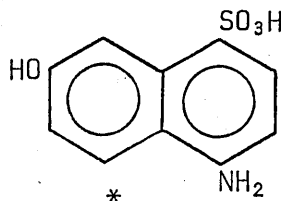
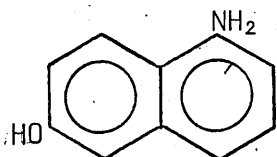


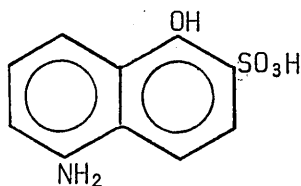
This compound was of immense interest at the start of the review period. The Author investigated several methods of preparation all of which involved at least one difficult stage and hence generally gave low overall yields. The two important properties of this isomer were:-

- (1) It coupled only once in the position ortho to the amino group.
- (2) The sulphonic acid group did not migrate to the -2- position.

As with isomer 461 a method of preparation was given by Roe and Thiot¹⁵ which was as follows:-

"1-Amino-6-naphthol sodium salt (181 parts), MnO₂ (240 parts) sodium bisulphite 32% (1500 parts by vol.) were heated at 55°C until no trace of 1-amino-6-naphthol. The mass was acidified and SO₂ removed, cooled and the 1-amino-6-naphthol-4-sulphonic acid (Isomer 471) filtered off. The yield was 60%."

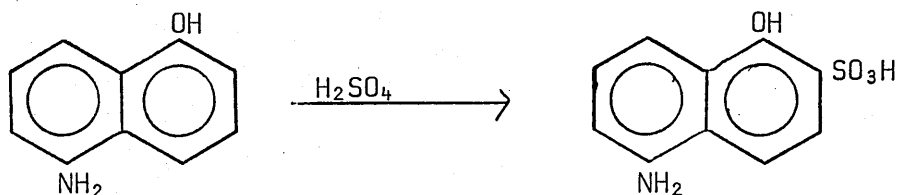


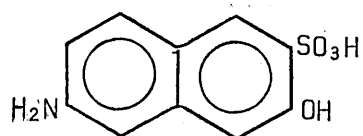


Two patents^{17,18} describe the preparation of "Magenta Images provided by Phenylazonaphthyl Dyes" in which one of the dyes utilised Isomer 512 and recorded its preparation in detail. The method was similar to previous recorded methods^{1,2} but will be described because it is more up to date and more detailed.

The method was described as follows:-

"1-Amino-5-naphthol (50g) was added to sulphuric acid (100g) below 30°C and stirred for 1 hour at room temperature; poured into ice (500g) and filtered off, and purified by solution in aqueous sodium carbonate and reprecipitation with acetic acid. The product was then digested in 2000ml water containing 100ml acetic acid, and after cooling yielded 48g (70% Theory)."

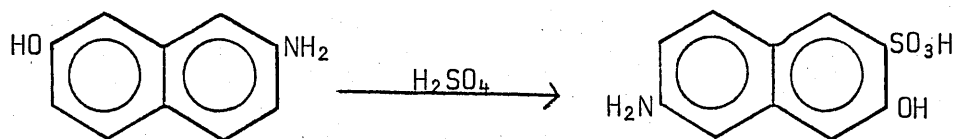




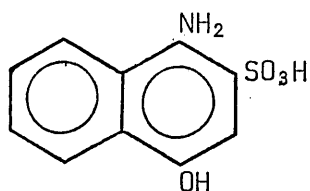
Jarkovsky¹⁹ disclosed the preparation of this isomer without quoting a yield as follows:-

"2-Amino-7-naphthol (10g) was added to sulphuric acid 98% (60g), kept at 100°C for 1½ hours, diluted with 25ml water and heated at 100°C for 2 hours, cooled, filtered and washed with water and then alcohol."

The Author also prepared this Isomer by heating 2-amino-7-naphthol with 90% sulphuric acid at 100°C.



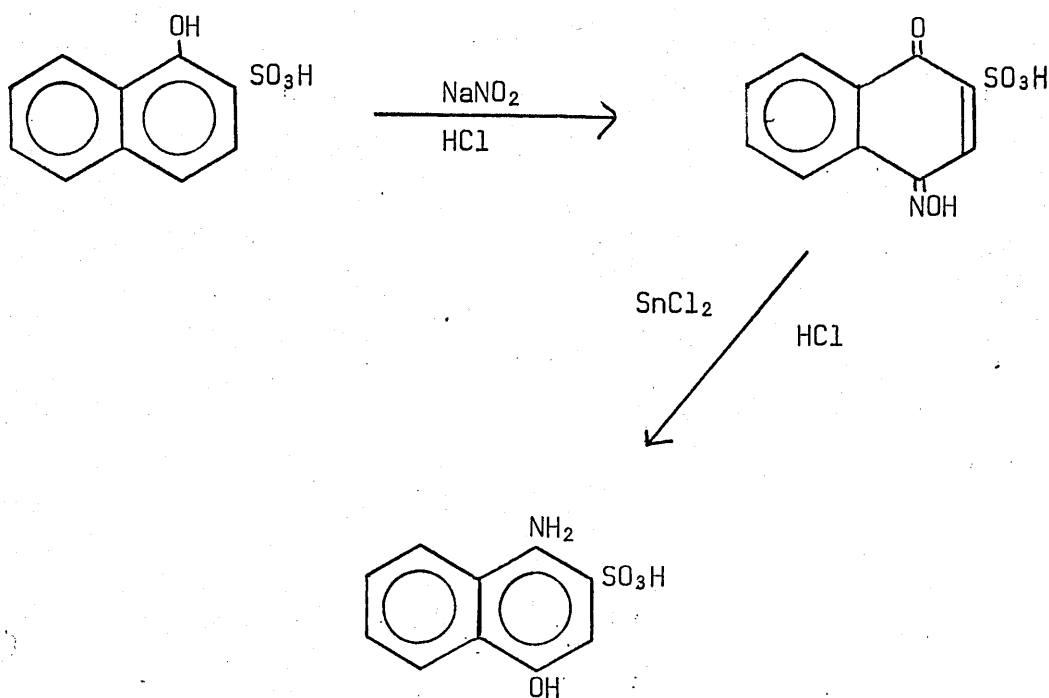
3.15 Isomer 142



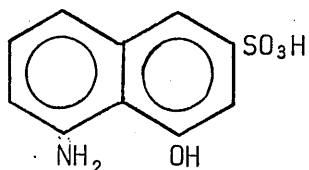
Bogdanov²⁰ described the preparation of this isomer, albeit with minimum details, as follows:-

"1-Naphthol-2-sulphonic acid when treated with aqueous nitrite and 12% hydrochloric acid at 25-30°C gave the yellow 1,4-naphthaquinone-2-sulpho-4-oxime. Reduction with SnCl₂-HCl gave 4-amino-1-naphthol-3-Sulphonic acid."

In the correct modern notation this latter compound would be written as 1-amino-4-hydroxy-naphthalene-2-sulphonic acid.



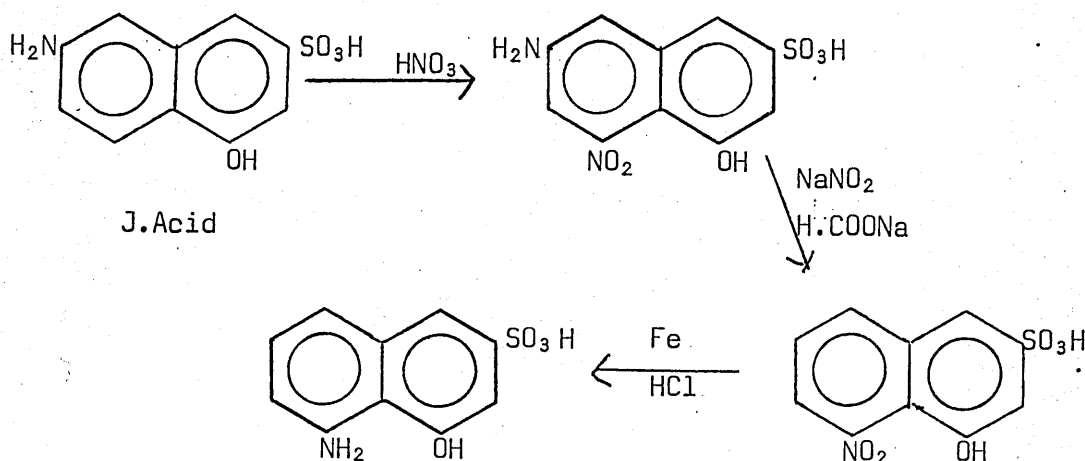
Isomer 142



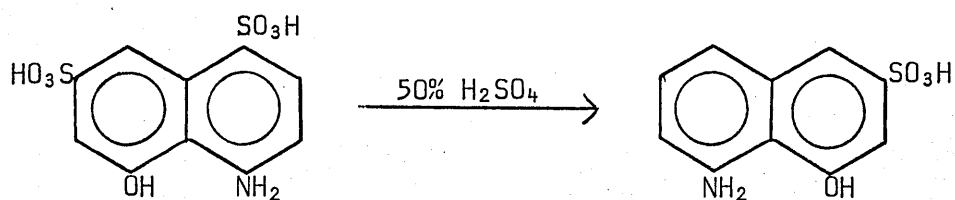
This isomer has been tested, not only as an intermediate for making azo dyestuffs, but as a catalyst, an indicator for nitrites and nitrates and as a base material for pharmaceutical products. However no other method of preparation has been given other than those in the pre-review references.^{1,2}

Nevertheless two potentially new methods can be suggested based on information available to the Author.

- (1) It was stated in Ako¹⁰ reports that J. Acid can be nitrated to give 7-amino-5-nitro-4-hydroxy-naphthalene-2-sulphonic acid. This compound can be de-aminated to 5-nitro-4-hydroxy-naphthalene-2-sulphonic acid which could be reduced using the standard iron reduction method to give the required isomer.

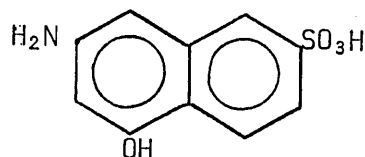


- (2) The Author has prepared this isomer by desulphonation of 4-amino-5-hydroxy naphthalene-1,7-disulphonic acid (K.Acid) by heating with 50% sulphuric acid at reflux for about 8 hours.²¹



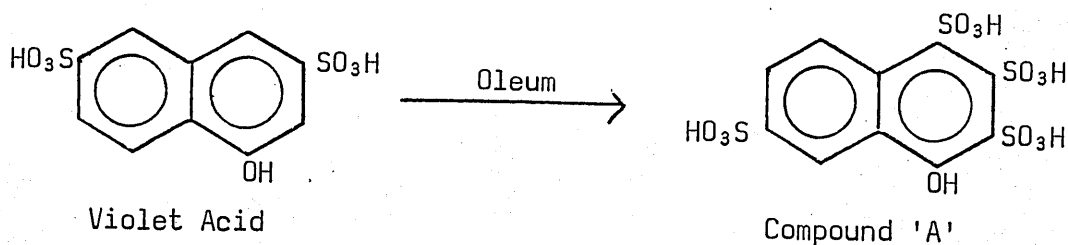
K.Acid

3.17 Isomer 752

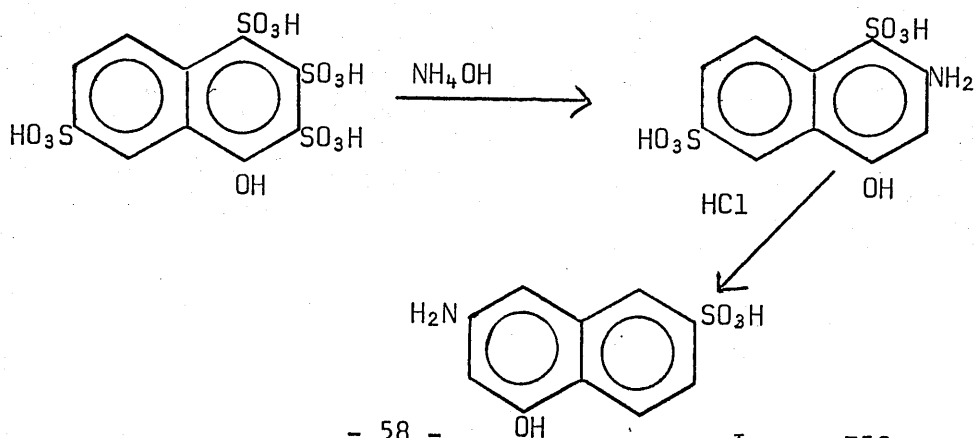


Blagney²² described a new method of preparation of this isomer as follows:-

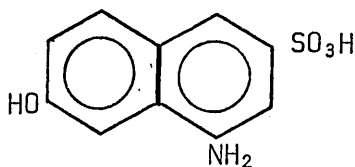
"4-Hydroxy-naphthalene-2,7-disulphonic acid (Violet Acid) (1200g, 4.5mol) was added slowly to Oleum 30% (1200g, 1.14mol) then heated to 125°C for 4 hours, poured onto Ice (4.5Kg) and isolated by salting with salt (600g), which precipitated the disodium salt of the compound 'A'.



Compound 'A' (55g) was heated with ammonia 25% (140ml) for 4 hours at 115°C which gave 2-amino-4-hydroxy-naphthalene-1,7-disulphonic acid mono sodium salt. This product after isolation was heated with hydrochloric acid and the required isomer was formed."



3.18 Isomer 462



Blagney²³ described a new method of preparation of the Isomer 462 as follows:-

Nitration of Naphth-(1,2)-oxadiazole-7-sulphonic acid

Naphth-(1,2)-oxadiazole-7-sulphonic acid (22.5g, 0.09mol) was charged with cooling into sulphuric acid 100% (110g). Then with ice and salt bath cooling, a mixture of nitric acid 40^oBe (10g) and sulphuric acid 100% (20g) was added dropwise below -5^oC and then stirred for 2 hours at that temperature. Small pieces of ice (110g) were added to precipitate the 9-nitro-naphth(1,2)-oxadiazole-7-sulphonic acid, which after filtration was washed with sulphuric acid 50% (60g) followed by a mixture of alcohol and ether and finally with ether, to give 21-21.5g (88% Theory) Product A.

Reduction of the Diazogroup

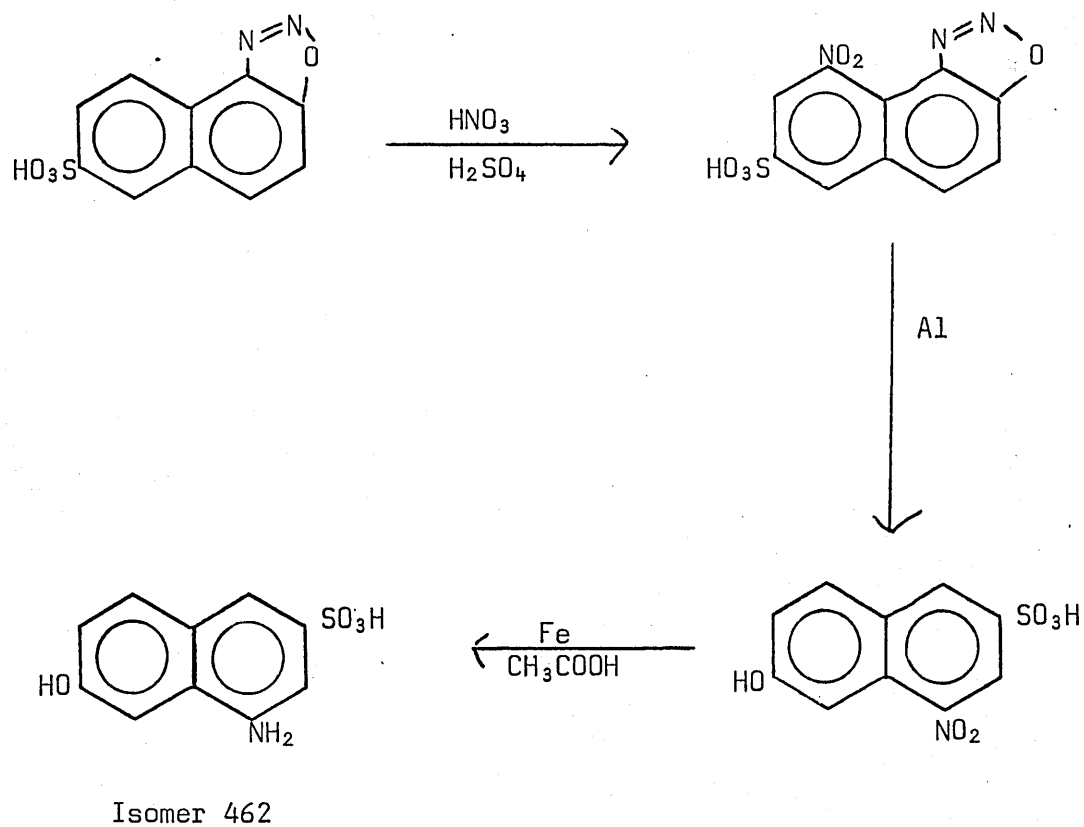
Product A (21.45g) was added to alcohol (200ml) in a distillation apparatus and aluminium powder (2.4g) added. 20ml alcohol was distilled off during one hour and then the reaction mass tested with Resorcinol (no colour reaction) to ensure the reduction was complete. The mass was filtered to remove impurities and the residues washed with hot alcohol. After concentration, potassium

chloride solution 25% (25ml) was added to precipitate the product, which after cooling was filtered, washed with potassium chloride solution then with alcohol and ether and dried in a steam oven to give 15.3g (60% Theory) 4-nitro-6-hydroxy-naphthalene-2-sulphonic acid.

Reduction of the Nitro Group

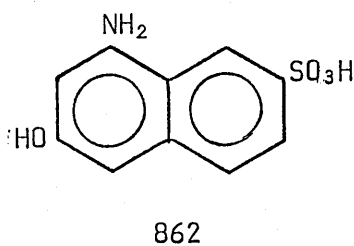
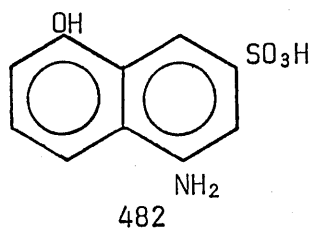
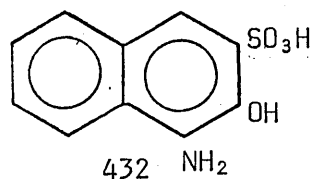
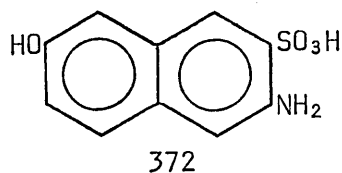
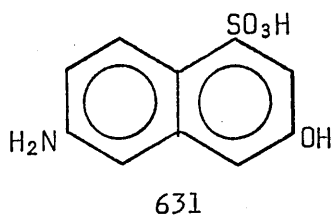
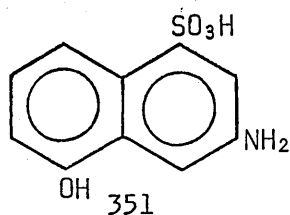
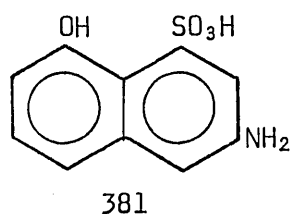
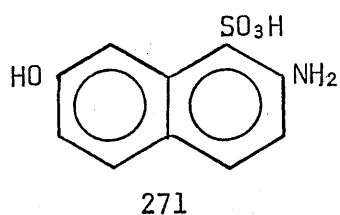
4-Nitro-6-hydroxy-naphthalene-2-sulphonic acid (7.23g) was charged slowly into a reduction vessel containing water (50ml) pin dust (7.5g) acetic acid 12% (7.5ml) maintained at its boiling temperature. When the reduction was complete soda solution 10.6% (10ml) was added, the mass filtered and the product precipitated by the addition of hydrochloric acid 36% (2.5ml). This was then cooled, filtered and washed with water, alcohol and ether and finally dried. The yield was 4.92g (87.4% Theory).

Blagney²³ does not give any indication of the potential hazard of this route. The Author, from his own experience, would stress that until hazard tests have been carried out on all the stages of this series of reactions, they must be assumed to be hazardous. This is especially true of the drying stage of the diazo compounds and the handling of the diazo compounds themselves. (See also comments in Section 4.5)

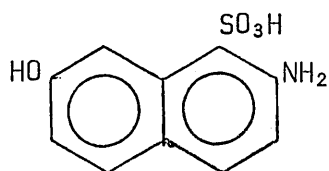


4.0 Isomers Recorded in the Literature after 1953

By examination of Tables 1 and 2, in Section 2 it was found that eight new isomers had been recorded in the period under review, these were:-



The method of preparation of each isomer has been given where recorded, and critically discussed where necessary. Where no method of preparation was given, the information available has been quoted together with suggested methods of preparation.



Two methods of preparation have been recorded, one by Jarkovsky¹⁹ and the other by Roe¹⁵.

4.1.1 Jarkovsky's Method

Jarkovsky described his preparation as follows:-

"2-Amino-7-hydroxy-naphthalene 51.2% (10g, .032mol) was added to sulphuric acid 98% (100ml) and kept at 0°C for 3 hours. This was then poured into ice (100g) and kept at 0°C overnight. The precipitate was filtered and washed with water and ethanol. Yield 3.75g."

The product, 2-amino-7-hydroxy-naphthalene-1-sulphonic acid, was identified by elimination of the amino group and comparing the resultant product with 7-hydroxy-naphthalene-1-sulphonic acid (Croceine Acid) chromatographically.

Jarkovsky also stated that this compound coupled with diazonium salts with difficulty.

Comments

The identity of this isomer is not as conclusive as it might at first appear. Jarkovsky failed to realise the possibility of sulphonation of the position ortho to the hydroxy group. This compound on deamination would give 2-hydroxy-naphthalene-1-sulphonic acid (Oxy-Tobias Acid). This compound also couples with difficulty, and under these conditions (Whatman No. 4 paper and eluted with 1-propanol, 5% NaHCO₃(2:1)) would have a similar R_f value to that stated.

To ensure that the characterisation was correct, the possibility of Oxy-Tobias Acid should have been eliminated by applying the ADAMS TEST which is specific for Oxy-Tobias Acid.

ADAMS TEST

A solution of diazotised 4-nitro-aniline is added to the test solution, and caustic soda liquor 32% added to make the solution strongly alkaline. If Oxy-Tobias Acid is present, a deep violet colour is formed which is discharged on heating.

4.12 Roe's method for Isomer 271

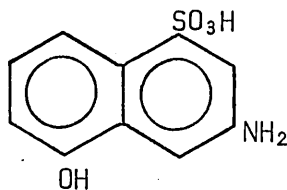
Roe described his method as follows:-

"2-Amino-7-hydroxy-naphthalene (159g, 1.0mol) was added to ethanol (600ml), water (3000ml), sodium

bisulphite 32% (400g, 1.23mol) caustic soda flake (40g, 1.0mol) and heated to 70°C. Manganese dioxide 85% (40g, 0.39mol) added and pH adjusted to 6.5-7.5 by the addition of sodium bisulphite; heated 16-20 hours at 70°C. Filtered, acidified and boiled to remove the alcohol and SO₂, cooled, filtered and washed with cold water. Yield = 191g 80% Theory"

Comments

No method of identification was given with this method, but sufficient examples of this type of reaction have been reported such that the reader should have some confidence that the compound was indeed the desired isomer 271.



There are two references to Isomer 351, both being the work of Bayer A/G^{24,25}, the latter being the most detailed. The base material 5-nitro-naphthalene-1-sulphonic acid has been manufactured for a long time, being formed as the minor isomer (22%) in the nitration of naphthalene-1-sulphonic acid. However, it has never been isolated as such. The separation from the major isomer (43%) was always done after the subsequent reduction stage. A direct method of preparation of this material would be the sulphonation of 1-nitro-naphthalene with oleum. However the manufacture of 1-nitro-naphthalene would now be banned because of the simultaneous production of 2-nitro-naphthalene which on reduction gives the carcinogen 2-amino-naphthalene (β naphthylamine)

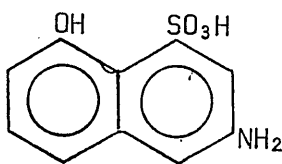
The Bayer process was described as follows:-

5-Nitro-naphthalene-1-sulphonic acid (50.6g, .2mol) was added at $10^{\circ} - 15^{\circ}\text{C}$ with cooling to oleum 20% (400ml) and KNO_3 (22g, .217mol) added at $10^{\circ} - 15^{\circ}\text{C}$. This was stirred 3 hours and poured into ice (2000g) at 20°C , KCl (200g) was added and the mixture stirred overnight. The resulting suspension was filtered and reduced with iron and the 3,5-diamino-naphthalene-1-sulphonic acid isolated with HCl and salt as an acid paste.

The acid paste (.1mol) and NaHSO_3 40% (200pts) was heated at $105-8^\circ\text{C}$ for 9 hours acidified to pH 3.0 at $50-80^\circ\text{C}$ and stirred to remove the SO_2 . NaOH liquor was added to give pH 10-10.5 and heated at $90-100^\circ\text{C}$ for 30 minutes. This was then acidified at 70°C and stirred until cold to give 3-amino-5-hydroxy-naphthalene-1-sulphonic acid.

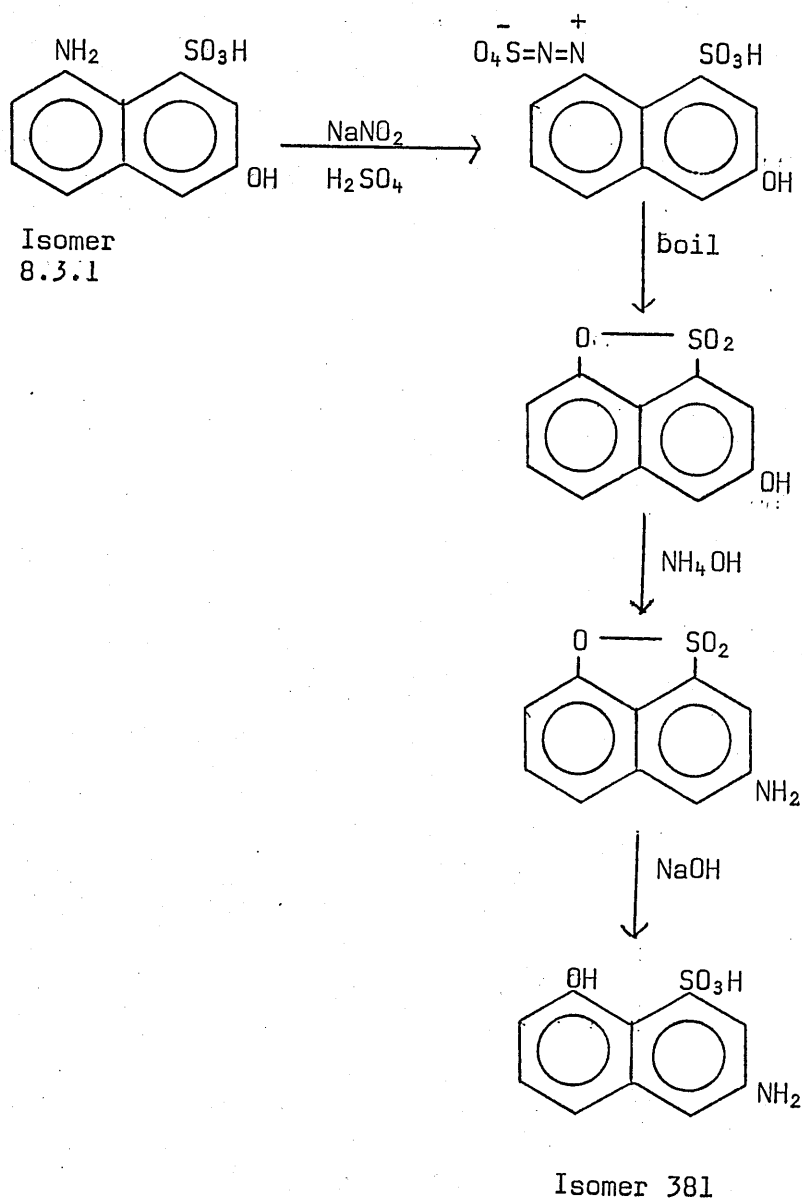
Comment

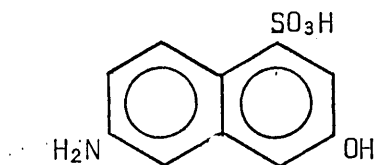
The final reaction is an excellent example of Bucherer's second rule. This states that an amino group in a position meta to a sulphonic acid group will not react with sodium bisulphite and hence only the 5-amino group was converted to a hydroxy group.



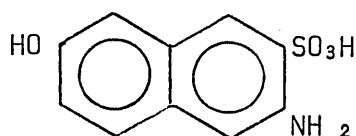
Cortes²⁶ described the preparation of derivatives of 2-hydroxy-1,3,2-benzodioxastibole one of which was derived from isomer 381. However, the preparation of isomer 381 was not included.

The following method is suggested as a possible route.

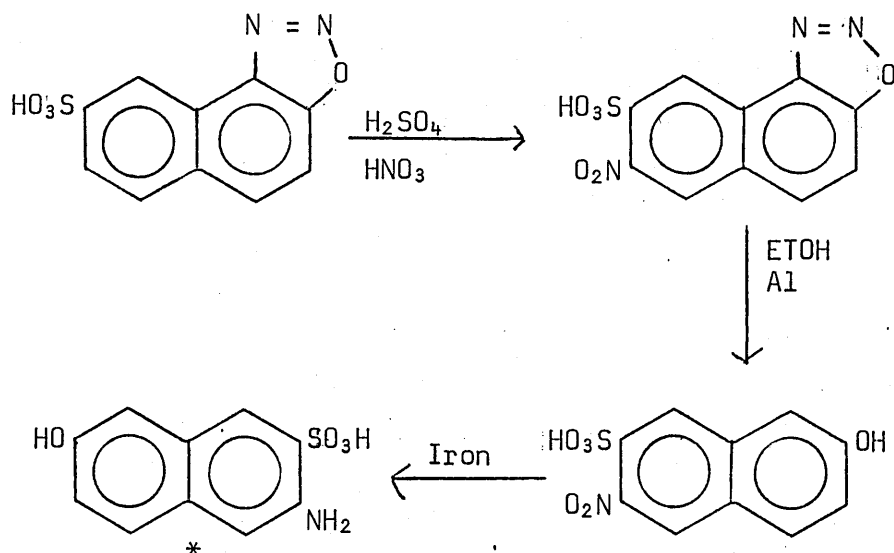




Todres²⁷ used X-ray crystallography to investigate the constitution of a compound which he had prepared and recorded in his thesis in Moscow in 1962. No method of preparation was given but the compound was shown to be isomer 631.



Blagney²³ prepared this compound by the nitration of naphth-(1,2)-oxadiazole-8-sulphonic acid, to give 7-nitro-naphth-(1,2)-oxadiazole-8-sulphonic acid. After isolation and recrystallisation from water, the product was treated with aluminium in ethanol to remove the diazo link, and then reduced with iron to give isomer 372.



The preparation details were reported as follows :-

"To 22.5g naphth-(1,2)-oxadiazole-8-sulphonic acid was added with cooling and stirring 110g conc. sulphuric acid, 10g (40⁰Be) nitric acid and 20g Monohydrate. The mixture was stored overnight at 0⁰C, and 110g ice added. After storing the mixture overnight at 0⁰C, the precipitate was collected by

filtration, washed with 60g sulphuric acid 50% and equal mixture of ethanol and ether and finally with ether. The yield was 21-21.5g of 7-nitro-naphth-(1,2)-oxadiazole-8-sulphonic acid.

This was charged into 200ml ethanol and heated with 2.4g aluminium to boiling and in the course of 1 hour, 20ml ethanol distilled off. The hot liquor was screened and concentrated to 50ml cooled and filtered off. The yield was 15.3g 2:6:7; $\text{HO}(\text{NO}_2)\text{C}_{10}\text{H}_5\text{SO}_3\text{H}$.

This on reduction gave 100% yield of 2:6:7

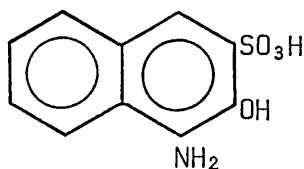
$\text{HO}(\text{NH}_2)\text{C}_{10}\text{H}_5\text{SO}_3\text{H}$ which was the required 3:7:2 isomer."

Comment

If the above preparation was attempted without reference to the original paper, a dangerous situation could arise. The procedure must be followed exactly; that is, the oxadiazole must be charged to the cooled sulphuric acid, the nitric acid and the monohydrate mixed and cooled and then added to the stirred mixture at -5°C .

From experience in the laboratory, oxadiazoles of this type do not nitrate easily under the above conditions, and must be stirred for several hours in the sulphuric acid medium before the addition of the nitric acid.

If this compound was being considered as a replacement for the manufactured isomer 431 (1:2:4 acid) special care would have to be taken as drying the oxadiazole could be hazardous. As an alternative, the water wet paste could be added to Oleum.²⁸ However, this would also present a number of hazardous problems which would have to be resolved before full scale trials could be undertaken.

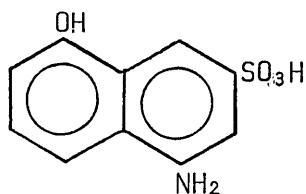


It is most surprising that this compound has not been previously recorded in the literature since it was extensively evaluated as an intermediate for Copper and Chrome Azo Dyestuffs 40-50 years ago by all the major dyestuffs manufacturers. It must be concluded that the products had no outstanding merit, or were too expensive to manufacture.

Two references appear for this compound one by Gasparie²⁹ and another by Osmann³⁰, both of whom used the isomer but gave no details of its preparation.

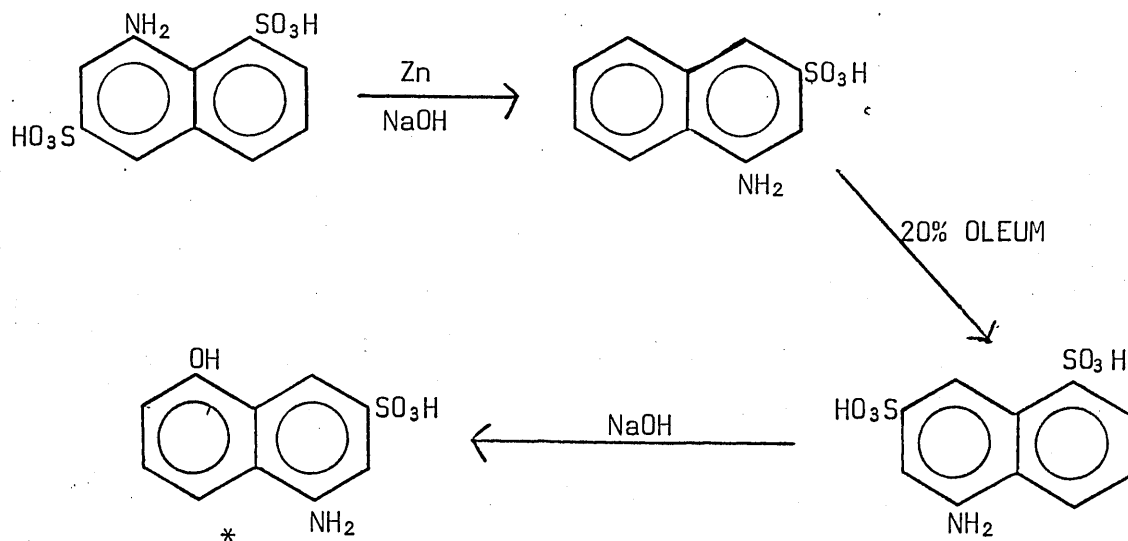
Many people have coupled diazo compounds with the intermediate 3-hydroxy-naphthalene-2-sulphonic acid³¹. The reduction of any of these dyestuffs with sodium sulphide, Hydros, or hydrazine⁹ would have given the isomer in good yield and quality.

4.7 Isomer 482



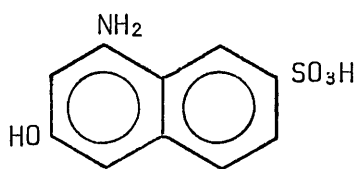
A Japanese Patent³² describes the use of this isomer in an admixture with basic dyestuffs to improve the dyeing properties of polyamide fibres, but gave no method for its preparation.

It is most probable that the following three stage processes were used, since the first two stages have been fully described in the literature^{33,34} and the final stage is similar to the J.acid fusion which is also well documented.



This isomer would be a useful intermediate for the dyestuff chemist, but would be very expensive because the base material 8-amino-naphthalene-1,6-disulphonic acid (1.3.8 Acid) is only produced as a 10% isomer in the manufacture of 8-amino-naphthalene-1,5-disulphonic acid (1.4.8 Acid).

4.8 Isomer 862



Gasparie²⁹ used this compound in chromatographic studies but did not disclose its method of preparation.

Cassella^{35,36} most probably prepared the isomer in 1890 when he described the "fusion of 1-naphthylamine-3,7-disulphonic acid with 40% caustic soda liquor at 200°C to give 1-amino-7-naphthol-3-sulphonic acid with a more soluble isomer."

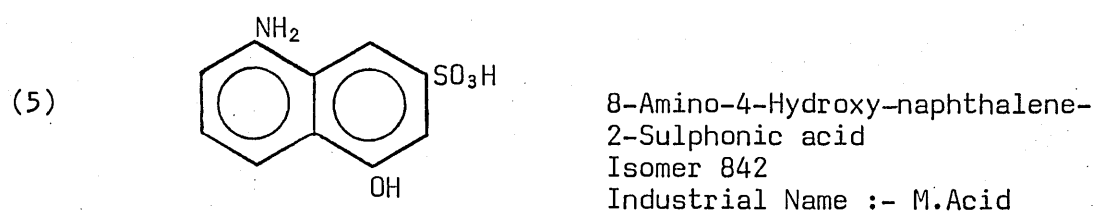
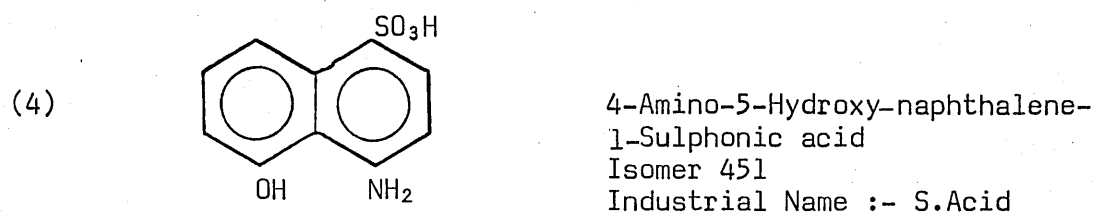
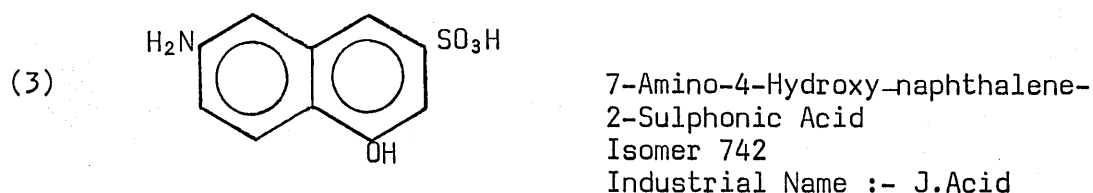
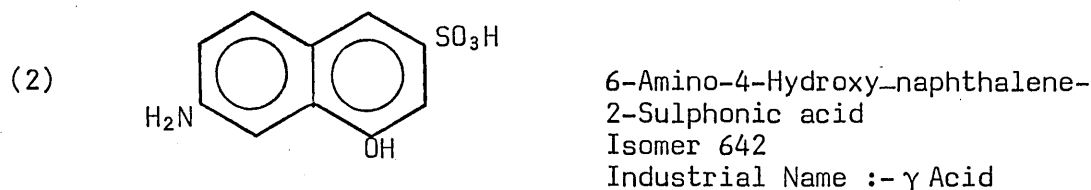
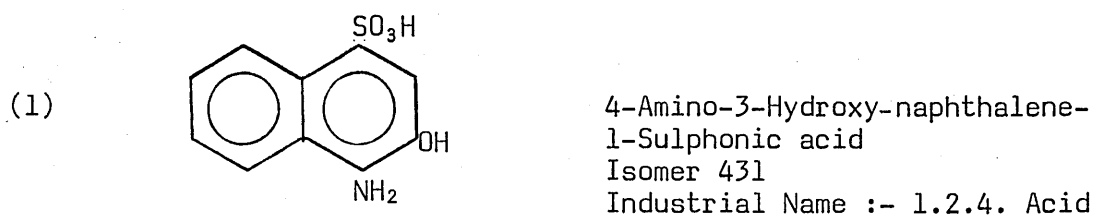
A further method was found in 'AKO' Reports¹⁰ which gave the following process as a direct method of preparation.

"1-naphthylamine-3,7-disulphonic acid was heated under reflux with 90% NaOH at 240°C in a stirred vessel, when pure 1-amino-3-naphthol-7-sulphonic acid was formed in 70% yield. The easily distinguished 1-amino-7-naphthol-3-sulphonic acid which was formed to some extent in the fusion process was not formed under these conditions. The base material was often impure and difficult to purify."

5.0 The 'Big Five'

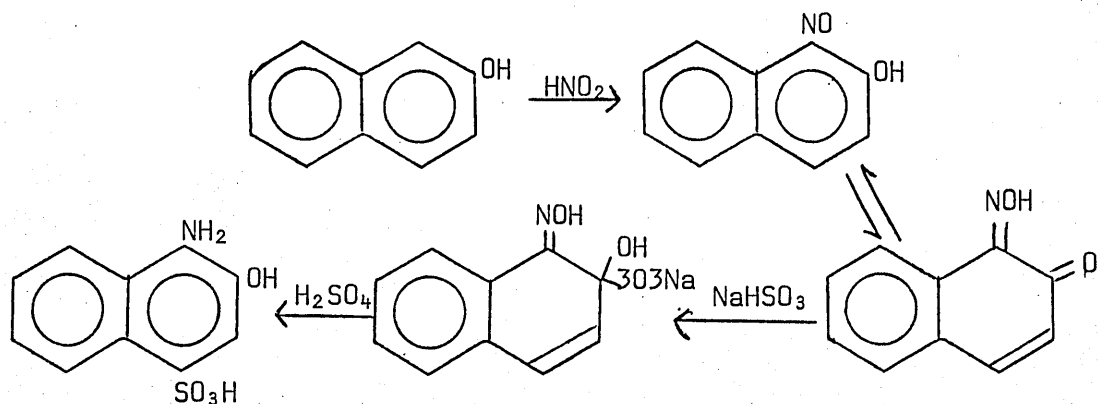
This section details (a) the original manufacturing processes of the five main amino-hydroxy-naphthalene-sulphonic acids together with any changes which have been made during the review period, and (b) other work and methods of preparation suggested in the literature.

The industrial names of these compounds have been used at all times in this section, and to ensure the reader is fully acquainted with them, they are repeated below:-



With the exception of M.Acid, which has only been prepared in the laboratory, the Author has been heavily involved with the manufacture of these Isomers from the base material Naphthalene up to the Isomer itself.

1.2.4 Acid was made by the Classical Chemical Reaction:-



5.1.1 Manufacturing Process²

2-Hydroxy-naphthalene (144g, 1mol) was added to water (900ml) and heated to 50°C , caustic soda 32% (125g, 1mol) was then added and stirred until it had completely dissolved.

Test 1

When one drop of this solution is added to Clayton Yellow Test Paper it should give a red colouration indicating that excess alkali is present.

Sodium nitrite (70.4g, 1.02mol) was dissolved in water (100ml) and run into the reaction mass, the volume being adjusted to 1500ml with ice and water such that the temperature was 0°C . Whilst maintaining this temperature, sulphuric acid 40% was added slowly during 3 hours until Test 2 was satisfied.

Test 2

When one drop of the reaction mass is added to Congo Red Test Paper, it should give a deep blue-black colouration, indicating a pH of less than 2.5.

The mass was agitated for one hour then filtered, and washed with cold water. The yellowish green 1-nitroso-2-hydroxy-naphthalene paste was used directly for the next stage of the manufacture.

The nitroso paste was added to water (500ml) and ice added to reduce the temperature to 5°C. Sodium bisulphite 40% (650g, 2.5mol) was then added as quickly as possible. A clear solution was obtained with a small amount of tar this being removed by screening. The temperature of the filtrate was adjusted to 25°C and sulphuric acid 30% (200g, .612mol) added during 1 hour. This was then stirred for 1 hour, heated to 50°C and allowed to stand without agitation for a minimum of 12 hours. The mass solidified to a cake, which was filtered and washed with cold water and dried. The yield was 215g (90% Theory).

5.1.2 Improvements Suggested in the Literature

Kolay³⁷ carried out a very detailed investigation into the use of various strengths of alkali. He concluded that the nitrosation was best carried out when the 2-hydroxy-naphthalene was in a highly dispersed state achieved by adding 0.8% dispersing agent and operated at a very high level of concentration. This gave an isolated yield of 1-nitroso-2-hydroxy-naphthalene of 90-93%.

Kolay also stated that the bisulphite compound required half to one hour to form at 18-20°C and that it was converted to 1.2.4 Acid by the action of sulphuric acid at 50°C over 2 days.

Zdenek³⁸ described a process for the continuous production of 1.2.4 Acid by feeding 1-nitroso-2-hydroxy-naphthalene and sulphuric acid into the bottom of a column, with sodium bisulphite as a downcomer. The internally formed bisulphite compound re-arranged and was extruded as a pasty product at the top of the column.

5.1.3 Comments and Suggestions

The process described in Section 5.1.1 had a number of drawbacks. It required a large number of vessels, involved three filtrations and finally allowed the product to solidify. The latter is of no consequence in the laboratory, but on the manufacturing scale this required men to climb into the vessel and dig it out!

A modern manufacturing process must not only be economically viable but also environmentally acceptable. In this process two gases were liberated and therefore the reaction vessels would have to be connected to the necessary gas adsorbers. Provided that the causes of the formation of impurities can be removed or prevented, the process is suitable for operating as a single stage process with only one filtration, that of the final product. This was achieved by making the following modifications:-

The caustic soda was added to the water and the temperature adjusted to 25°C. The 2-Hydroxy-naphthalene was sieved in to eliminate lumps which would not dissolve, and stirred until a complete solution was obtained. Commercial strength sulphuric acid (B.O.V. 78%) was

added below the surface of the mass to reprecipitate the 2-hydroxy-naphthalene at an even rate over several hours. This gave a very fine suspension which was easy to nitrosate, without the use of a dispersing agent.

The sodium nitrite was added as a solid and agitated to dissolve before the sulphuric acid was added slowly below the surface such that no fumes were emitted, there was no frothing, and on test, no 2-hydroxy-naphthalene remained unreacted.

The conversion of the nitrosation mass to the 'Bisulphite' compound free of tar was achieved by adjusting the mass to its effective temperature and pH and on adding the sodium bisulphite, a clear solution indicated a successful reaction.

The modernisation of the rearrangement stage, that is the conversion of the 'Bisulphite' compound to 1.2.4. Acid was very difficult to achieve. The days of men climbing into vats to dig out a solid product are past and gone as are the processes which involved holding vats at 50°C for 2 days. Theoretical consideration of this reaction indicated that it was exothermic. When this was taken into account and a more suitable pH chosen the reaction time was reduced to 5 hours. By gently stirring this, a mobile mass was obtained, which could then be de-gassed by prolonged agitation prior to filtration and washing. The laboratory yield was obtained in manufacture, this being of the order of 85%.

5.1.4 Other Literature Methods

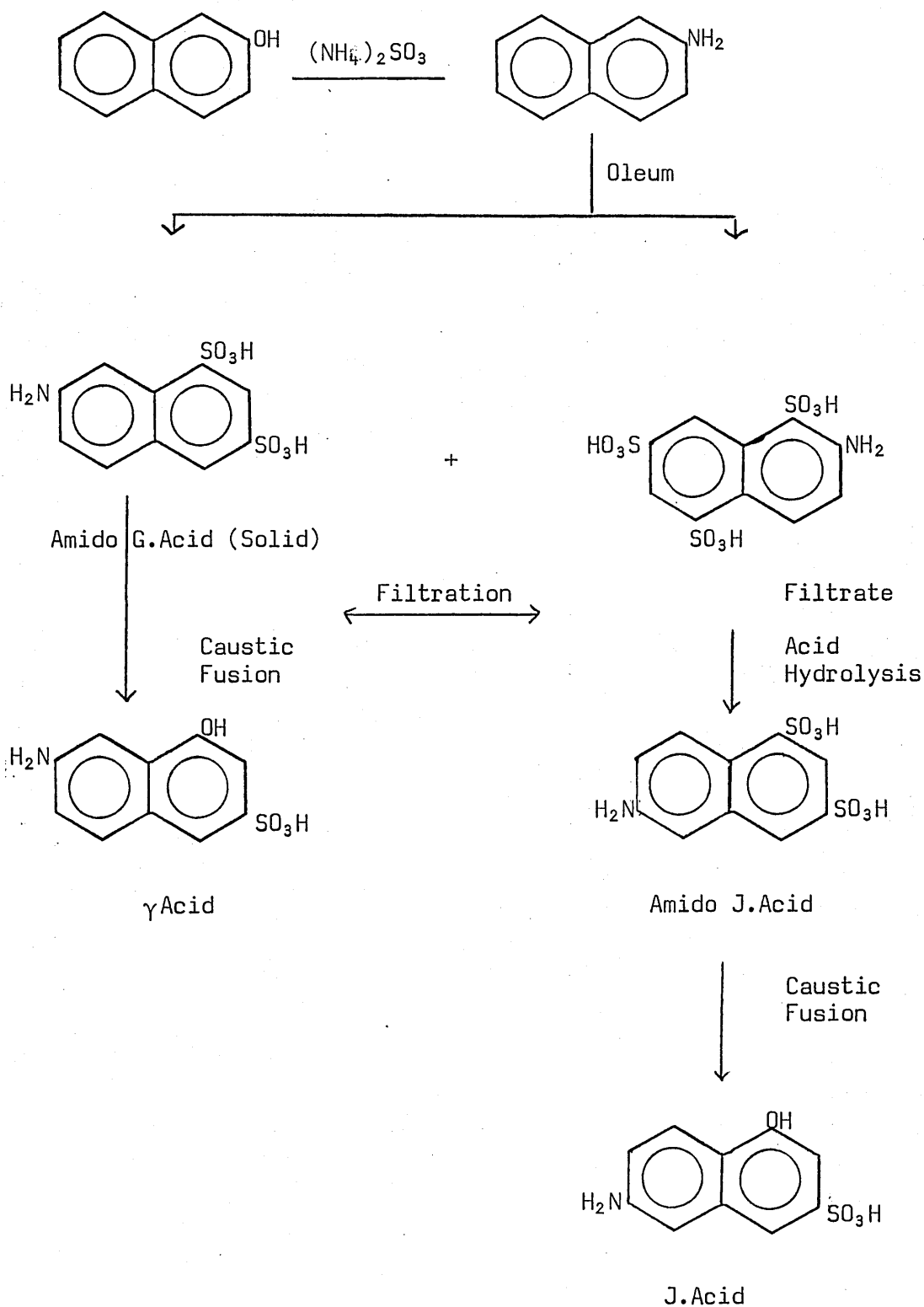
Baman and Schriever published several papers^{39,40,41} dealing with the oxidation of naphthylamine (sulphonic acids) using ozone, manganese dioxide and sodium metabisulphite. This route however to 1.2.4 Acid lacked commercial potential.

The Bayer patent¹³ referred to in Section 3 was also used for the preparation of 1.2.4. Acid. However, the coupling component 3-hydroxy-naphthalene-1-sulphonic acid is usually obtained from 1.2.4 Acid itself, thus this is not a viable route. Nevertheless the Tooke method⁹ which uses hydrazine hydrate could be a practical way to reduce the Dyestuff obtained from 3-hydroxy-naphthalene-1-sulphonic acid now that hydrazine hydrate has become available at an economic price.

5.1.5 Conclusion

The literature has little to offer in the way of a potential manufacturing process, and although Kolay and Zdenek have made definite progress, they only considered part of the process. To be of real value they should have dealt with the reaction as a whole.

Until about 1954-1955, γ Acid and J. Acid were manufactured by the '2-Amino-naphthalene' process. Thereafter separate processes were used for each compound. The original process is shown below:-



5.2.1 The Problem Associated with 2-Amino-naphthalene

The reason for the drastic change of manufacturing processes was the cessation of the production of 2-amino-naphthalene, brought about by a change in the Industrial Climate and pressure of public opinion.

Many men who had operated the 2-amino-naphthalene plants or who had been involved with its use, had died from cancer; thus its effects were well known. Initially the manufacturers did not withdraw the compound but built open air plants to safeguard the men, but in fact this was probably a bad decision because the land and buildings outside the plant were then contaminated. The Author was seconded to one such plant as a shift chemist but because of the terrible hazard, with youthful diligence, was able to opt out within a few weeks. The plant operated for about 10 more years.

Although the scourge of 2-amino-naphthalene was well known, other compounds which contained it were considered safe. The Author was again involved in research work on the preparation of amino-hydroxy-naphthalene-sulphonic acids based on 2-amino-naphthalene-1-sulphonic acid (Tobias Acid)⁴² which unknown to him contained free 2-amino naphthalene.

A further source of 2-amino-naphthalene was from the manufacture of 1-amino-naphthalene. The nitration of naphthalene produced 1-nitro-naphthalene contaminated with 2-nitro-naphthalene which after reduction was separated out as 2-amino-naphthalene.

The Author was again involved with this process in about 1965 when he devised and developed a process for the safe removal of 2-nitro-naphthalene by a method involving the Janovsky Reaction⁴³. However, before this became operational, a member of the plant staff died from cancer and the plant was closed never to re-open.

Some 10 years ago there was another public outcry when it was revealed that a Rubber Company was found to be using imported 2-amino-naphthalene.

With the help of t.I.C., g.l.c., and h.p.l.c., it is now possible to detect the presence of this and other carcinogenic compounds present as impurities and to take positive action to remove them or to cease their manufacture. The effort of companies to do this was revealed in a series of American Cyanamid Patents⁴⁴⁻⁵⁰ describing methods of reducing the 2-amino-naphthalene content in Tobias Acid to a level of 13ppm. A letter from American Cyanamid to the Author stated that they have now ceased all such manufacture.

5.2.2 Manufacture of γ Acid by the '2-Amino-naphthalene' Process

This has been included because of its historic value and to enable a comparison to be made with the present day process.

2-Amino-naphthalene from 2-Hydroxy-naphthalene

2-Hydroxy-naphthalene was charged into an autoclave containing ammonia and ammonium bisulphite, the autoclave sealed and heated to 150°C for 8 hours. This was then discharged into water, when the

product was separated as an oil. The oil was washed with hot water under pressure, then vacuum distilled and the product 'Flaked'.

Sulphonation of 2-Amino-naphthalene to Amido G.Acid

The 2-Amino-naphthalene was charged into Oleum 20% at a temperature below 35°C and stirred until a sample was completely soluble in dilute sodium carbonate solution. Oleum 65% was added and the mixture heated to 70°C for 1 hour, then 95°C for 15 hours. This was then cooled and discharged into ice and water giving a final temperature of 20°C. The 7-amino-naphthalene-1,3-disulphonic acid (Amido G.Acid) was precipitated and filtered off. The filtrate contained 2-amino-naphthalene-1,5,7-trisulphonic acid which was transferred to the J.Acid unit. The Amido G.Acid paste (1mol) was charged into water at 95°C sodium carbonate (1mol) added followed by lime until the mass was just no longer acid to Congo Red Test Paper.* The gypsum was filtered off and washed with hot water. The filtrates were then made alkaline with sodium carbonate, the chalk filtered off and the liquors concentrated to 60%. The Amido G.Acid disodium salt was now ready for fusion to γ Acid.

*Note: The pH maybe 3-6.5 but must not be allowed to become alkaline as this would destroy the physical form of the gypsum.

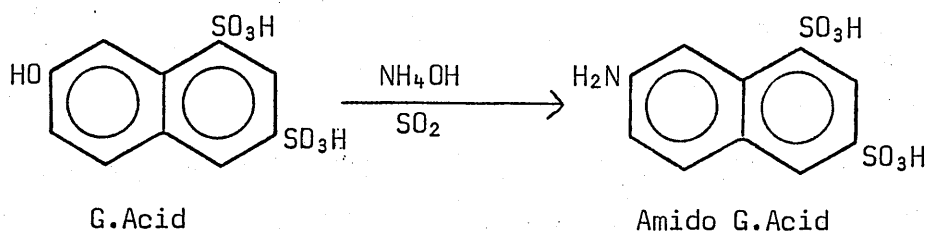
5.2.3 Fusion of Amido G.Acid to γ Acid

Sodium hydroxide 75% (427Kg, 8mol) was run into an autoclave and heated to 175°C. Amido G.Acid 60% (1.3mol) was run in at 175-180°C over 15 hours and the water allowed to evaporate such that the volume at the end of the addition was 550 l. The autoclave was then sealed and heated to 205°C for 7 hours. This was then cooled, the pressure released and the mass diluted with water and blown into dilute sulphuric acid. After the removal of the SO₂ the batch was cooled filtered and washed. Yield 90%

5.2.4 Replacement Process for the Manufacture of γ Acid

Very little further work was required to develop this new process. A very good manufacturing process for 7-hydroxy-naphthalene-1,3-disulphonic acid (G.Acid) already existed, so all that was required to be developed was a Bucherer reaction on the G.Acid to give Amido G.Acid. The Amido G.Acid could be converted into γ acid using the fusion reaction employed in the previous process.

The process was as follows:-



Ammonia 28% (4mols) was charged into an autoclave and the dipotassium salt of G.Acid (1mol) added as a 60% paste followed by SO₂ (.3mol). The autoclave was then sealed and heated to 180°C for 18 hours. The reaction mass was then blown into a distillation vessel containing caustic soda (1mol) and the ammonia distilled off and recovered for re-use. The liquor was then evaporated to 60% and used directly for the fusion to γ Acid. The yield was 97-98%.

The process had in fact been used by some manufacturers to supplement the manufacture of γ Acid. It was employed when the demand for γ Acid had exceeded that which was obtained from the 2-amino-naphthalene process and the manufacturers did not wish to stockpile J.Acid.

5.2.5 Literature Information

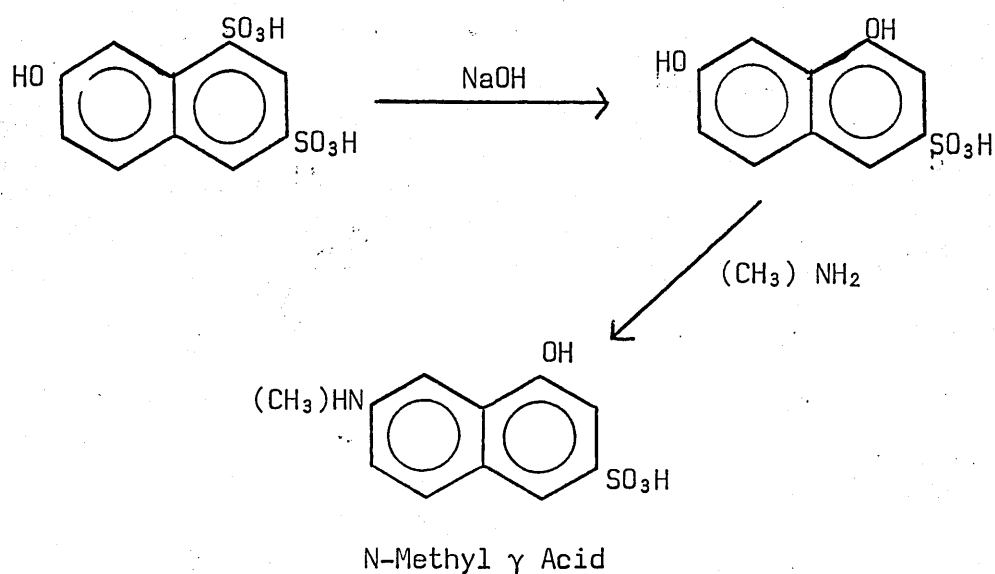
A continuous process⁵¹ has been described which gave a yield of 98% and purity 99%. The reaction was carried out in a special titanium plated reactor where the ratio of reactants and the temperature of the reaction were similar to those in the above process.

A Ciba-Geigy general patent⁵² for the manufacture of γ Acid, J.Acid, 2R Acid and other hydroxy-naphthalene compounds claimed high yields of γ Acid (91%). In this case the fusion temperature was 185-90°C, when 4mols of caustic soda were used per mol. of Amido G.Acid, the reaction time was not less than half the charging

time and the water content between 0.5-20%. This method was also suitable for use as a continuous process.

5.2.6 Other Suggestions

There is a further method of preparation of γ Acid but no mention of it in the literature could be found. This process was used for the preparation of N-Methyl γ Acid and is as follows:-



This method could be used for γ Acid if ammonias is substituted for methylamine.

5.2.7 Conclusions

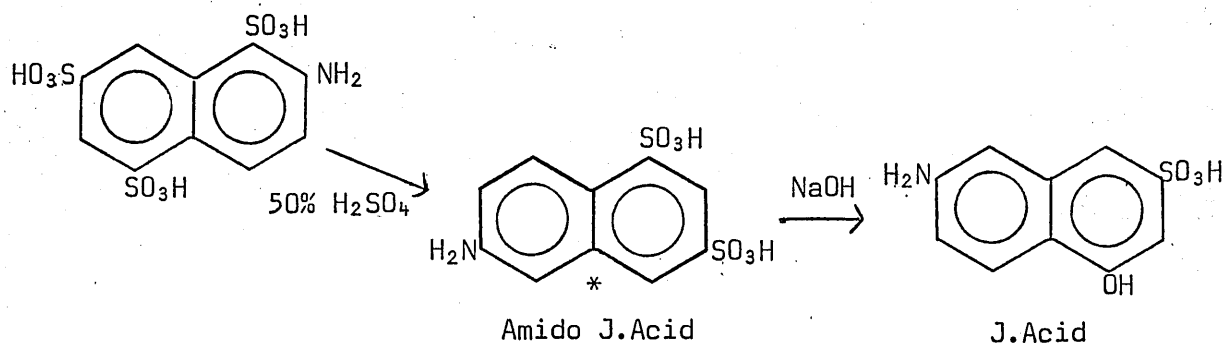
There is still much interest in the manufacture of γ Acid, as shown by the two patents. However the aim of the work is to standardise the process such that several products can be manufactured in the same plant. This contrasts with the practice of 50 years ago where each product had its own plant.

The high yields attained in the Bucherer and Fusion stages leave little or no scope for a further improvement in the reactions themselves. This was demonstrated by the use of the classical conditions in the projected processes described in the patents.

J.Acid has been the most important isomer since it was first prepared. The manufacture has caused the death of many workmen and even today the literature reveals that major manufacturers are still concerned with the presence of 2-amino-naphthalene formed during its manufacture.

5.3.1 Manufacture by the '2-Amino-naphthalene' Process

The process was as follows:-



The filtrates from the Amido G.Acid process (Section 5.22) were diluted with water such that the Sp.Gr. was 1.3 and heated to 105°C for 3 hours. The reaction mass was then cooled to 20°C, filtered and washed with dilute sulphuric acid. This was then converted to the di-sodium salt. The acid paste was charged into water at 95°C, and 1mol/mol* of sodium carbonate added. After neutralising with lime, the gypsum was filtered off. The filtrate was then made alkaline with sodium carbonate, the chalk filtered off and evaporated until the Amido J.Acid content was 60%. The Amido J.Acid was then ready for fusion.

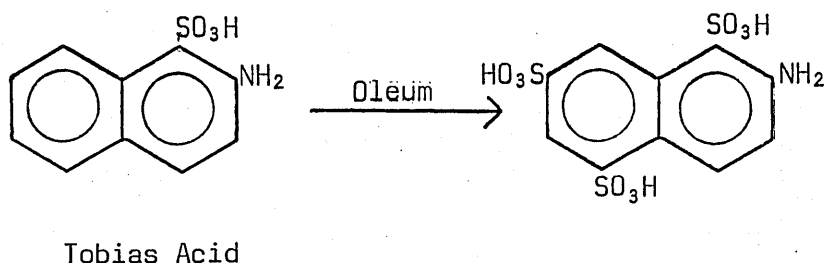
* One mol of sodium carbonate for each mol. of Amido J.Acid

Sodium hydroxide 75% (4.5mol) was run into a fusion vessel, heated to 175°C and the Amido J.Acid (1mol) run in during several hours at 175°C. The water was allowed to evaporate, and the mass then heated to 185°C until the reaction was complete. The mass was diluted with water and the product isolated by acidifying with sulphuric acid. The yield from 2-amino-naphthalene was about 40% and from Amido J.Acid 85%.

5.3.2 Replacement Process for the Manufacture of J.Acid

When the replacement process was being considered, it was found that a completely new process was not required.

Only the first part of the process to produce 2-amino-naphthalene-1,5,7-trisulphonic acid needed to be developed and this was achieved by changing the base material from 2-amino-naphthalene to 2-amino-naphthalene-1-sulphonic acid (Tobias Acid) which when sulphonated gave the required 2-amino-naphthalene-1,5,7-trisulphonic acid.



Tobias Acid was a manufactured product but not on the scale required for making J.Acid and therefore the Tobias Acid process needed to be re-developed. Similarly a new process was required for the sulphonation stage.

5.3.3 The Manufacturing Process for Tobias Acid

The old process consisted of adding 2-hydroxy-naphthalene to nitrobenzene, cooling to 0°C and whilst at this temperature adding chlorosulphonic acid over several hours. The product was then extracted with water, converted to the sodium or ammonium salt and aminated with ammonia and SO₂ to give the required Tobias Acid.

5.3.4 Literature Information

American Cyanamid⁴⁴⁻⁵⁰ described the above process at a temperature of 7°C either batchwise or as a continuous process.

Arai⁵³ described the sulphonation in sulfolane using SO₃ as the sulphonating agent.

Stasek⁵⁴ found that nitrobenzene could be replaced by 2-nitrotoluene.

A recent patent⁵⁵ described the use of 'A water anhydrous solvent' such as 1,2 dichloro ethane at a temperature of 0-10°C and this was the only reference to a commercial process which did not use nitrobenzene. This was most surprising since it was well known in industry that a very cheap non-toxic solvent was indeed being used instead of nitrobenzene. Soon after the process involving this latter solvent was established, there was a major panic when the solvent manufacturers announced that it was to be removed from their manufacturing range. Major development

programmes were initiated to find yet another solvent but all were unsuccessful. However, for some unknown reason, the problem did not arise and the use of the solvent continued.

The Ciba-Geigy patent⁵⁵ also stated that the hydrochloric acid produced in the sulphonation was removed by vacuum, when normally it was removed by air blowing. This change in procedure could be very important since the aim of all process developers had been to make the Oxy-Tobias Acid free from hydrochloric acid so that it could be converted to the ammonium salt and used as such in the amination to Tobias Acid.

If hydrochloric acid was present, ammonium chloride was formed and this sublimed, blocking the safety release valves thus making the process unacceptable.

Solvent processes of this kind differ from an ordinary sulphonation in that no excess of sulphonating agent is required. An excess of agent in the above process would produce the unwanted 2-hydroxy-naphthalene-1,6-disulphonic acid.

A good manufacturing process⁵⁶ for the amination stage has been described in detail and used commercially. This process involved the amination of Oxy-Tobias Acid with ammonia and SO₂ at 150°C at 8-10 ats. The ammonia was recovered by discharging the amination mass into a slurry of lime. This also converted the SO₂ into calcium sulphite which was filtered off. The liquors were acidified to give Tobias Acid.

American Cyanamid⁴⁴⁻⁵⁰ used a similar process but at the lower temperature of 117-123°C and claimed a yield of 87-95%. The ammonia

was recovered by blowing into aqueous caustic soda and this solution then acidified to recover the SO_2 and to precipitate the Tobias Acid.

Stasek⁵⁴ described a similar process at 150°C but claimed a yield of only 77%.

Plattner⁵⁵ used only ammonia for the amination. Bayer⁵¹ however described two processes one without SO_2 at $120^\circ\text{--}125^\circ\text{C}$ and one with SO_2 at $135\text{--}145^\circ\text{C}$ both processes gave a yield of 97%.

The replacement process, which used one of the above systems did not however completely solve the problem relating to the presence of 2-amino-naphthalene. For example, American Cyanamid⁴⁴⁻⁵⁰ extracted their product with toluene to reduce its content from 443ppm to 13ppm. This was not the only problem associated with this process, an explosion occurred in a Tobias Acid Aminator⁵⁷, causing the death of the operator.

5.3.5 Sulphonation of Tobias Acid to 2-Amino-naphthalene-1,5,7-trisulphonic acid

No problem was experienced with this stage, the same conditions being used as those for the sulphonation of 2-amino-naphthalene (Section 5.2.2) although the final temperature was increased to 110°C .

A Russian patent⁵⁸ gave the following process:-

"Tobias Acid was sulphonated in a two stage process with 20-24% Oleum at $94\text{--}96^\circ\text{C}$ and at $113\text{--}118^\circ\text{C}$ for

second stage. The reaction mass was hydrolysed with aqueous sodium sulphate at 103-110°C."

The Author has no knowledge of a hydrolysis with sodium sulphate solution. As the latter would be difficult to remove from the precipitated Amido J.Acid its presence in the subsequent fusion to J.Acid would cause great difficulties with the agitation of the mixture. The hydrolysis would be carried out exactly as in the old process as given in Section 5.3.1 i.e. diluting with water such that the Sp.Gr. was 1.3 and heated to 105°C for 3 hours.

5.3.6 Literature Information on the Fusion of Amido J.Acid to J.Acid

The fusion process described in Donaldson² was still being used at the end of this review period. It was known that when caustic potash was substituted for caustic soda the temperature could be reduced by some 20°C and the mass was more fluid. This however was not operated because of the high cost of the caustic potash.

A Russian patent⁵⁸ described the fusion at 175-185°C and the isolation by acidification with sulphuric acid. Ciba-Geigy's general patent⁵² for J, γ , and S. Acids described a continuous process with a yield of 91%.

American Cyanamid⁵⁹ described a novel method for the fusion as follows:-

"caustic soda (15.2g,.05mol), water (1.5g, .083mol), Amido J.Acid (15.2g,.05mol) and Sulfolane (4.4g) heated to 210°C then 15 minutes at 270°C gave J.Acid 9.6g = 80% yield."

A similar process⁶⁰ used phenol as the diluant as follows:-

"Amido J.Acid 70.2% (.1mol) containing sulphuric acid (.042mol) was mixed with phenol(.23mol) and caustic soda (.96mol) and heated under nitrogen to 270°C for 5 minutes, cooled, diluted with water, poured into excess sulphuric acid. The resultant product contained J.Acid (16.5g) Tobias Acid (.4g), and the filtrate contained J.Acid (2.9g), Tobias Acid (.98g) and Amido J.Acid (1.44g). The overall yield was 81%."

The two processes above were obviously developed to produce a continuous process and had achieved a fair degree of success. The use of phenol is no problem in the laboratory but on the manufacturing scale would be Hazardous.

5.37 Comments and Conclusions

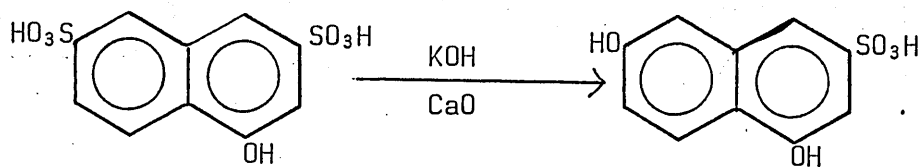
The J.Acid process was a long and exacting process which required a vast and expensive manufacturing unit. In keeping with the other isomers, the direction of modernisation of this process was towards the introduction of continuous processes.

When working on the J.Acid process the Author often looked for a new route to J.Acid which would be simple and eliminate the formation of 2-amino-naphthalene. Two possible methods were from time to time considered but were never actively followed up. They are as follows:-

- (1) The solvent sulphonation of a modified form of 2-hydroxy-naphthalene to give the required 2-hydroxy-naphthalene-1,5-disulphonic acid or even the-1,5,7-trisulphonic acid.
- (2) Fusion of naphthalene-1,3,6-trisulphonic acid to 4,7-dihydroxy-naphthalene-2-sulphonic acid which could then be aminated to J.Acid by the Bucherer reaction.

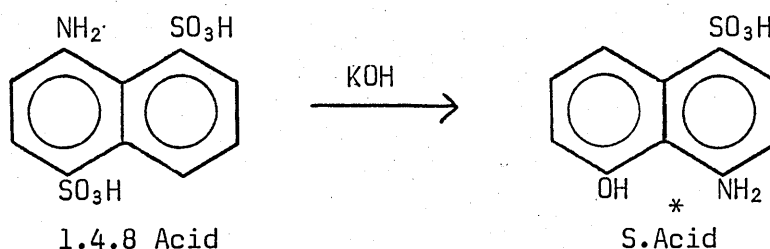
The second method offered the best prospect for success because naphthalene-1,3,6-trisulphonic acid was a manufactured product and a process for its fusion to 4-hydroxy-naphthalene-2,7-disulphonic acid (Violet Acid) was well established. The further fusion of Violet Acid had been attempted¹ but was reported to cleave the

disubstituted ring at the temperature required for the reaction. If the 4,7-dihydroxy-naphthalene-2-sulphonic acid could be formed the subsequent amination to J.Acid would not have produced 2-amino-naphthalene. With this in mind the literature was examined to see if this latter route had been evaluated during the review period. It was discovered that a Japanese patent⁶¹ describing the manufacture of 1-hydroxy-naphthalene also stated that the route was used for the preparation of 4,7-dihydroxy-naphthalene-2-sulphonic acid. This was achieved by fusing Violet Acid with a mixture of potassium hydroxide and calcium oxide at 290°C for 5 minutes. This again was an obvious candidate for a continuous process.



If this reaction worked in the laboratory and gave a good yield, then at first sight, it could be the breakthrough which had been sought for so many years. However, whilst this route might be satisfactory in the laboratory, on the manufacturing scale there would be a very serious problem. Throughout all the work on the fusions of naphthalene sulphonic acids, care must be taken to remove any traces of calcium ions from the fusions. If this is not done layers of calcium sulphite would build up on the sides of the autoclaves reducing the rate of heat transfer and so preventing the reaction from reaching the correct temperature.

The manufacture of S.Acid differed from the manufacture of the other 4 members of the 'Big Five' in that it was the only one stage process, namely the alkali fusion of 8-amino-naphthalene-1,5-disulphonic acid (1.4.8 Acid). The latter was commercially available as it was also used in the manufacture of Azo Dyestuffs.



S.Acid was required for the manufacture of Azo Dyestuffs and therefore had to be of a consistent quality. This quality was often very difficult to achieve because towards the end of the fusion process the Amino group began to react to give 4,5-dihydroxy naphthalene-1-sulphonic acid. This impurity was very very difficult to remove by the usual methods of purification. Zaviyalon⁶² described a method of purification using wood charcoal, but, from the Author's experience this treatment was only of superficial value.

5.4.1 Manufacturing Process

The first process that was recorded² stated that the 1.4.8 Acid was fused with caustic potash at 210°C whilst other sources¹ reported that the 1.4.8. Acid was fused with caustic soda 73% at 175°C until the reaction was complete.

Both these processes appeared to be a little unrealistic. The former is too drastic and the latter too low in temperature. The fusion of an α sulphonic acid group (Section 1.1) normally required a temperature of 185-190°C so a temperature of 190-195°C would be thought to be more realistic.

5.4.2 Literature Information

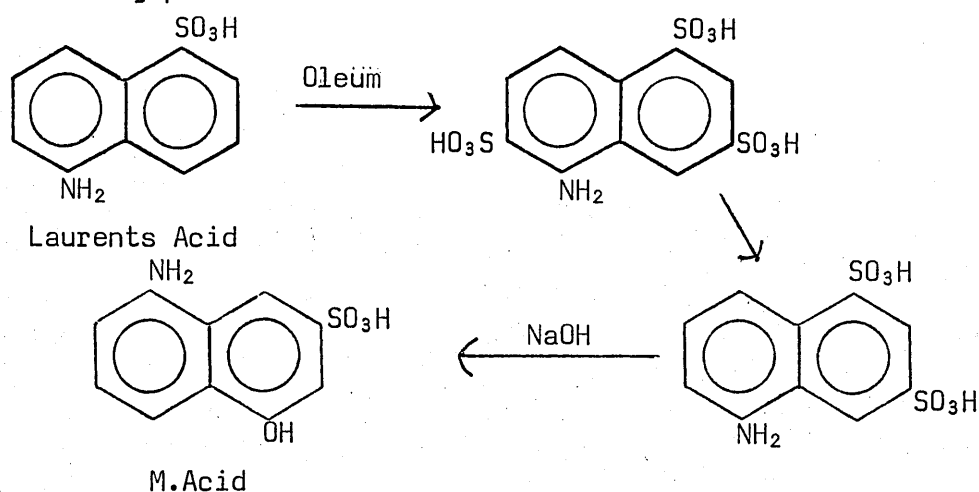
No method of preparation or manufacture was recorded in the literature until 1978 when a general patent by Ciba-Geigy⁵² described a batch or a continuous process. This was suitable for the fusion of naphthylamine-sulphonic acids containing 2 or more sulphonic acid groups. In this process the water content was maintained between 0.5-20% and the reaction time was not less than half the mixing time. The example was as follows:-

"Caustic soda 75% (213g, 4mol), 1.4.8. Acid disodium salt (347g, 1mol) in water (127g) were simultaneously metered during 3½-4 hours into caustic soda 75% (106g, 2mol) at 185-190°C with continuous distillation of water, then heated at 190°C for 3½-4 hours, diluted with water, neutralised with sulphuric acid to give 88% yield."

This process fitted the expected procedure, but from the Author's experience it was never possible to quote an exact length of time for the reaction. The completion of the reaction had to be

approached with great care, being sampled and tested after 3 hours and from the results obtained the extra heating time estimated based on previous experience.

M.Acid was manufactured only in Germany using the following process.²⁸



"Sulphuric acid 100% (603g, 6.15mol), Oleum 24%

(737g, 2.2mol) were mixed and cooled to 20°C.

Laurents Acid 93.7% (105g, .65mol) added below

30°C, Oleum 65% (420g, 3.4mol) added below 40°C

cooled to 20°C. Laurents Acid 93.7% (105g, .65mol)

added below 30°C. Oleum 65% (420g, 3.4mol) added

below 40°C and stirred 4 hours at 40°C; poured into

water (3500ml) and evaporated to give a B.P 130°C

and refluxed for 10 hours, cooled, filtered,

washed, recharged into Water (500ml) neutralised

with caustic soda, made just acid to Congo Red

Test Paper and filtered. Yield of 1-naphthylamine-

5,7-disulphonic acid 72.3%

Caustic soda flake (100g, 2.5mol), water (39ml)

mixed and heated to 170°C, 1-naphthylamine-5,7-

disulphonic acid (196g, .4mol) added over half an

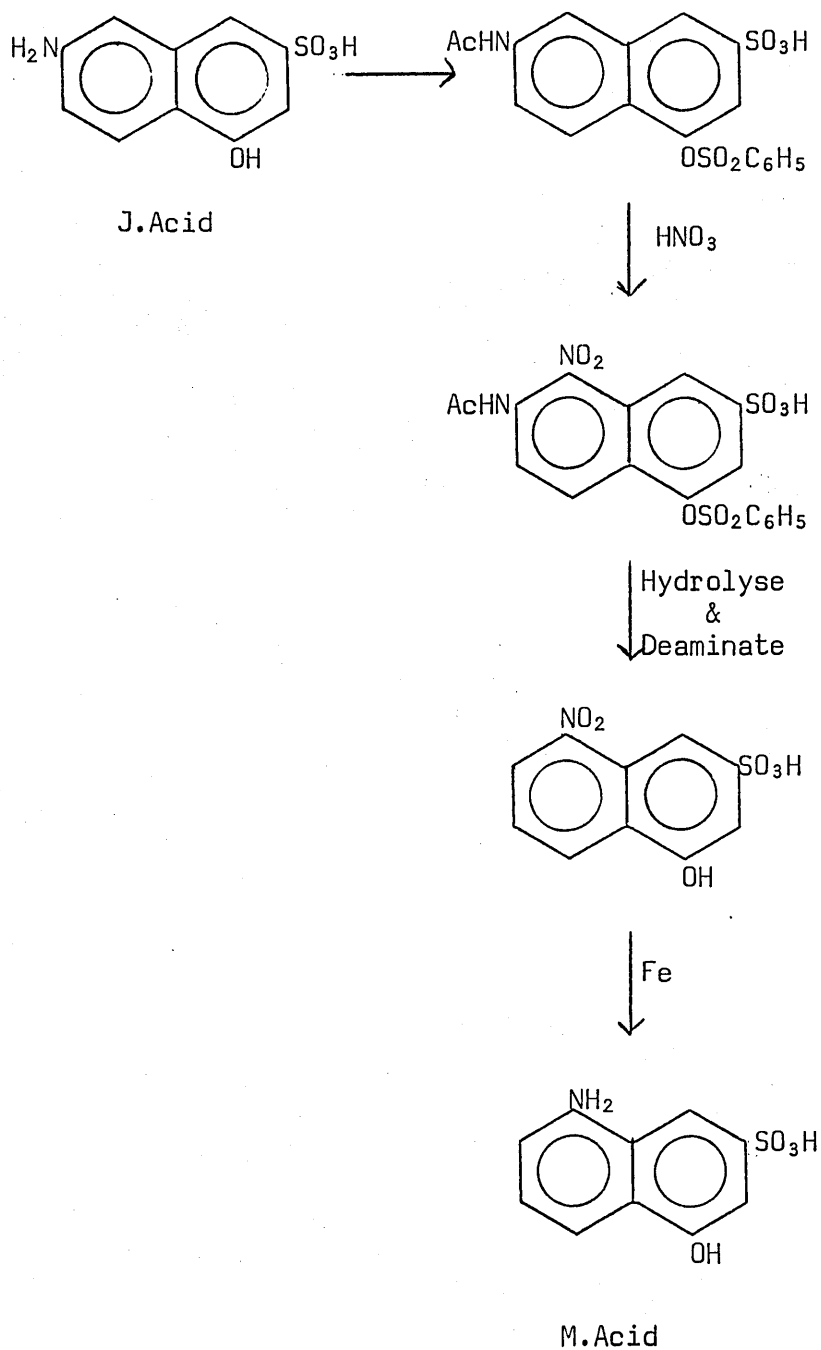
hour held 2 hours at 175-180°C, diluted with water (300ml) and poured into water (600ml), acidified at 80°C SO₂ boiled off and the M.Acid filtered hot and washed with hot water. Yield 78%."

5.5.1 Comments

M.Acid was probably considered to have greater commercial potential than other isomers because its constitution was similar to J. and γ Acids (Section 1.6) although there was perhaps another reason. Laurents acid was obtained as a 20-23% by-product in the manufacture of 8-amino-naphthalene-1-sulphonic acid (Peri Acid) and was often never isolated but run to waste. By converting it to M.Acid it was hoped to avoid this waste. There was however always the problem that if it became a big seller, the only way to meet the demand would be by making Laurents Acid from naphthalene-1,5-disulphonic acid by fusion and Bucherer reaction. This however would have been uneconomic.

5.5.2 Literature Information

A literature search has produced no further information on the manufacture of M.Acid. However the following information was found in 'AKO' reports¹⁰ and may have been an attempt to avoid the shortage of Laurents Acid. No actual details were given but the result was considered very interesting but of doubtful economic value.



M. Acid was still tested as a dyestuffs component from time to time⁵⁴ but with no apparent commercial success.

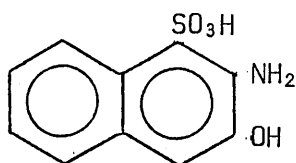
6.0 Suggested Methods of Preparation for the Unknown Isomers

25 isomers have not been named or methods of preparation reported in the literature as shown in Section 2. Five of these isomers have been prepared in the laboratory, and full experimental details are given in Section 7.

The remaining 20 isomers are listed below and methods of preparation are suggested for each one.

<u>Isomers</u>	231	571	132
	241	621	312
	261	671	352
	281	681	382
	321	761	532
	361	821	732
		861	762

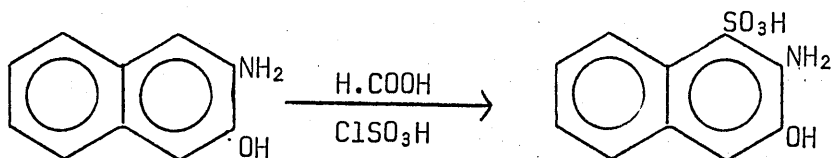
6.1 Isomer 231



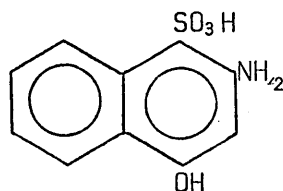
The method described by Jarkovsky¹⁹ (Section 4.1) for Isomer 271 had to be considered but as with Isomer 271 it was rejected because it did not agree with the Author's experience.

The suggested method is as follows:-

2,3-Amino-naphthol (1 mol) was charged into 1,2-dichloro-benzene (750ml) and formic acid (3ml) was added as a catalyst. chlorosulphonic acid (1mol) was then run in slowly allowing the HCl to escape. When the addition was complete the temperature was raised to give a steady reflux and this was maintained until no more HCl was liberated.¹⁶ The product was extracted with an aqueous solution of caustic soda and the product isolated by the addition of hydrochloric acid.



6.2 Isomer 241



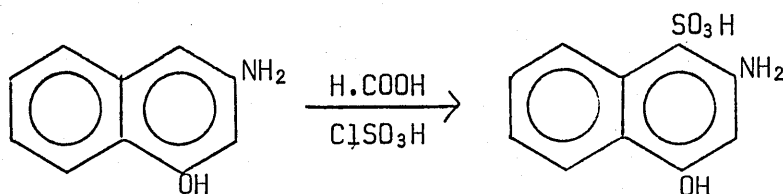
There are three methods of preparation which can be suggested for this isomer, these are:-

- (a) Jarkovsky's method¹⁹ which again would be rejected.
- (b) The same method¹⁶ as given in Section 6.1 but using 2,4-amino-naphthol as the base material.
- (c) This method is considered a good possibility.

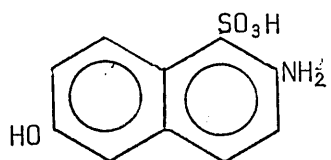
It is based on the work of Roe and Thiot¹⁵ and is as follows:-

2,4-Amino-naphthol is added to a mixture of ethanol, caustic soda, and sodium bisulphite and to this mixture is added at pH 7.0-7.5 manganese dioxide and reacted for 20 hours.

Method (b)



6.3 Isomer 261

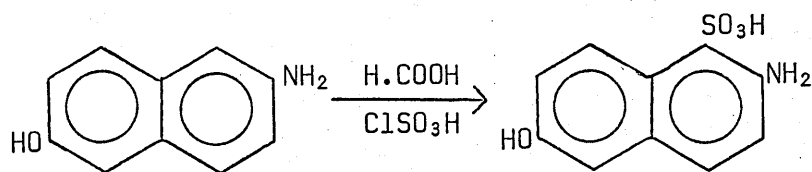


Methods (b) and (c) in Section 6.2 are suggested for this isomer also. The base material would be 2,6-amino naphthol.

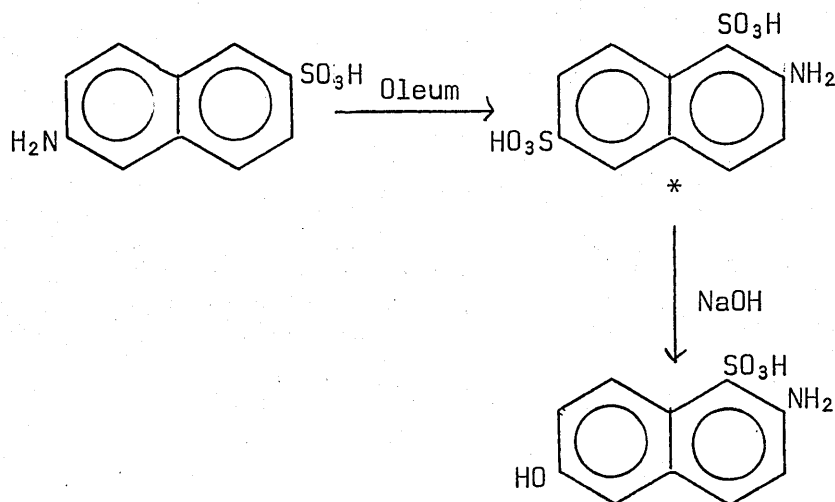
A further suggestion would probably be made at a 'Think Tank' session on the following lines:-

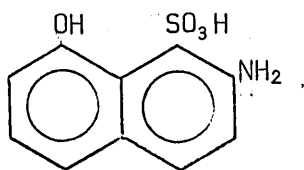
Sulphonate 6-amino-naphthalene-2-sulphonic acid to give 2-amino-naphthalene-1,6-disulphonic acid and fuse this with caustic soda to give Isomer 261. It is possible that this method might give a very small amount of the product and worth a try if none of the other suggested methods had worked.

Method (b)

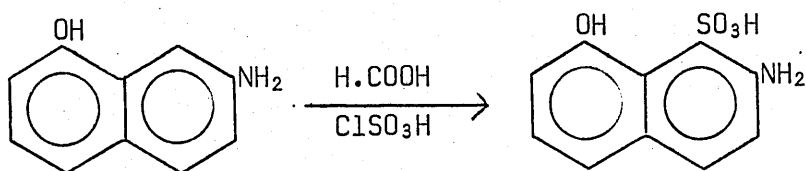


Method 2

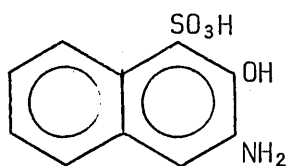




This isomer would be very difficult to make. It is again suggested that methods (b) and (c) in Section 6.2 be again tried using 2,8-amino-naphthol as the base material.

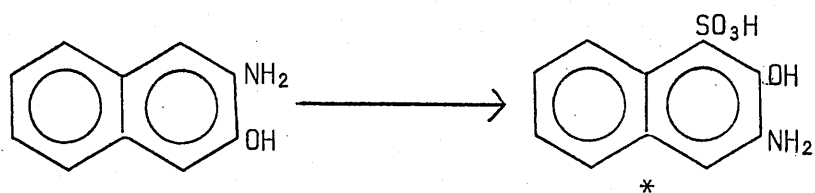


6.5 Isomer 321

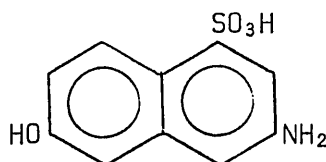


This is considered the easiest of the unknown isomers to prepare. The following method of preparation should give the correct product.

2,3 Amino naphthol (16g, .1mol) was added to sulphuric acid 90% (160g), and stirred for 5 hours at 10-20°C. The mixture was then poured very slowly into a mixture of ice and water (500g) keeping the temperature below 5°C by the further addition of ice as was necessary. The product was filtered off and washed acid free with cold water. This product could be identified by eliminating the amino group and testing the remaining solution for 2-hydroxy-naphthalene-1-sulphonic acid (Oxy-Tobias Acid) by the Adams Test (Section 4.1).

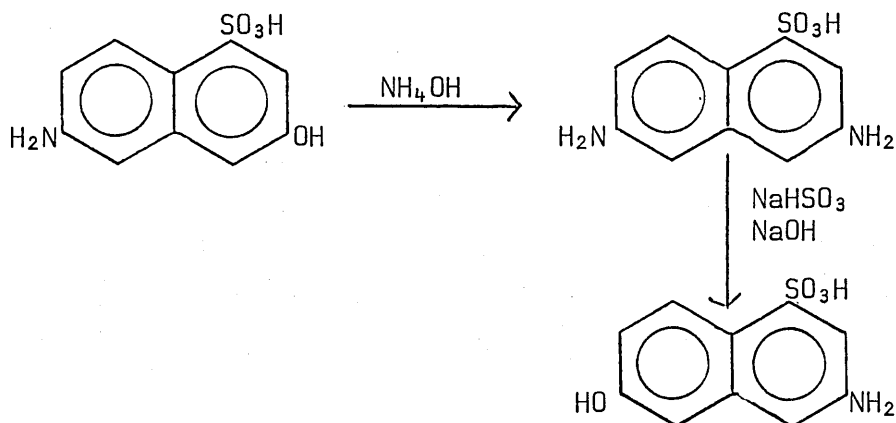


6.6 Isomer 361



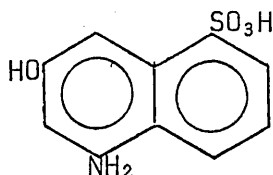
This is considered the most useful of the unknown isomers. It is however, very difficult to prepare and therefore not surprising that no one has attempted its preparation. The following synthesis is suggested.

Todres²⁷ prepared and identified isomer 631. By taking this isomer as base material and submitting it to the following series of reactions, the required isomer would be made.



The amination stage could not be by the Bucherer reaction because the hydroxy group is in meta position to the sulphonic acid group. A method developed by the Author for difficult amination⁶³ would probably be required. The final Bucherer reaction would be an example of this classical method.

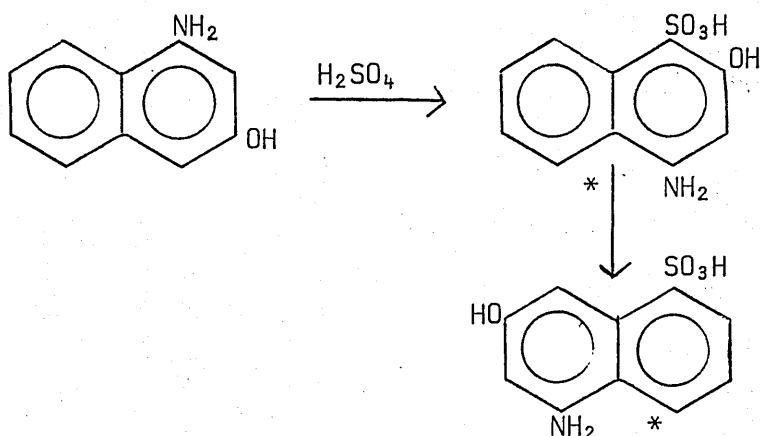
6.7 Isomer 571



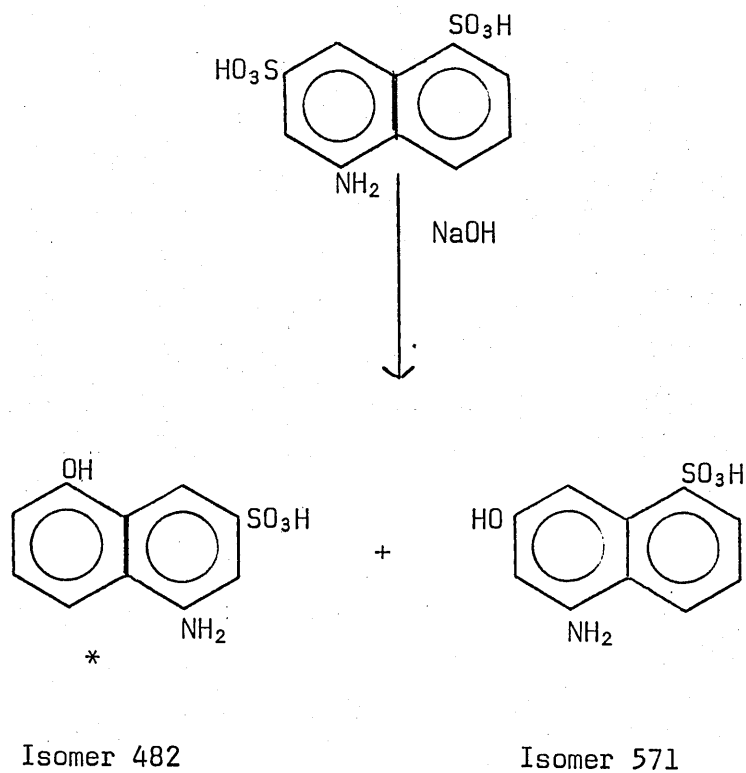
In Naphthalene Chemistry, one very useful reaction is the 'Migration or Isomerisation' of a Sulphonic Acid group.⁶⁴ This has already been referred to in Section 3.11. It is used commercially in the manufacture of 1,3,6-naphthalene-trisulphonic acid when the unwanted 1,3,5-naphthalene-trisulphonic acid impurity is isomerised to the required 1,3,6-compound.

The method proposed for Isomer 571 utilises this isomerisation procedure, and is as follows:-

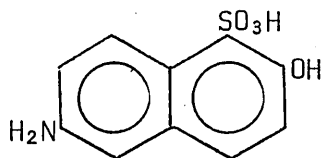
1-Amino-3-hydroxy-naphthalene was added to sulphuric acid 90% at 10°C, and stirred until t.l.c. tests indicated that no base material remained. The temperature was then raised over 4-5 hours to 100°C, and held until t.l.c. tests indicated that the compound formed at 10°C had been isomerised into a different compound, which should be the required Isomer 571.



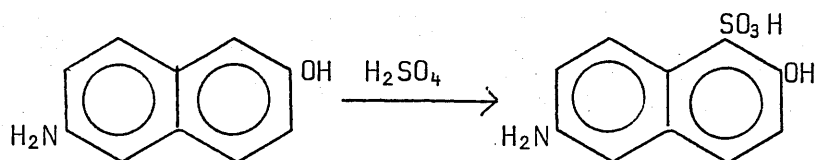
A second method is the fusion of 5-amino naphthalene-1,7-disulphonic acid (1.3.5 Acid) with 75% caustic soda at 195-200°C. The main product will be Isomer 482 but there would probably be a small amount of the Isomer 571.



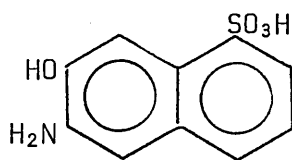
6.8 Isomer 621



The suggested method of preparation of this isomer is the cold sulphonation of 2-amino-6-hydroxy-naphthalene with sulphuric acid 90% at 10°C. The product would be isolated by pouring the sulphonation mass into a mixture of ice and water with good agitation to ensure that the temperature never exceeded 5°C.

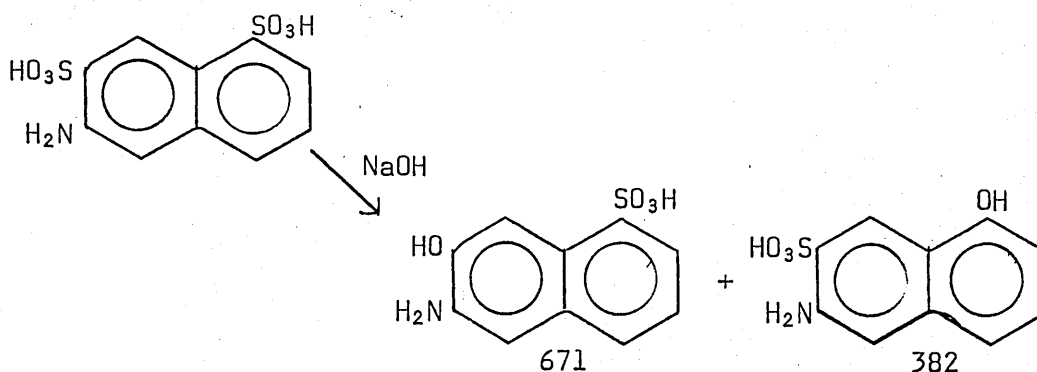


6.9 Isomer 671

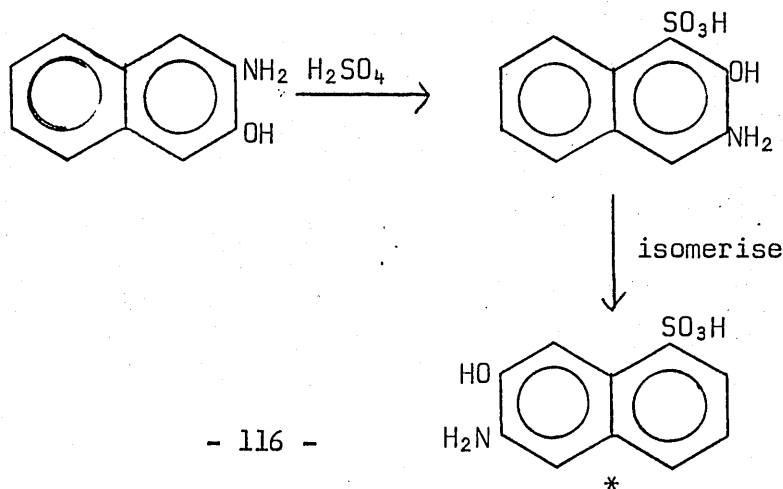


Three methods of preparation are suggested for this isomer, but the first two will only give the isomer in very small quantities.

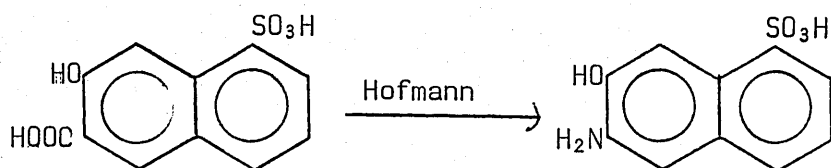
The first method is to fuse 6-amino naphthalene-1,7-disulphonic acid which had been isolated by Petitcoles⁶⁵ with caustic soda 75% at 190-200°C when a mixture of Isomers 671 and 382 (Section 6.17) would be expected to be formed. Isomer 382 would be the main component



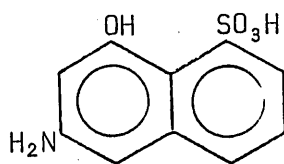
The second method is the sulphonation of 2-amino-3-hydroxy-naphthalene with sulphuric acid 90% at 10°C, and then heat to 100°C over 5 hours to isomerise the sulphonic acid group into the required position.



The third method and probably the best, is to carry out a Hofmann Reaction on 7-hydroxy-6-carboxy-naphthalene-1-sulphuric acid, which would give the required product.

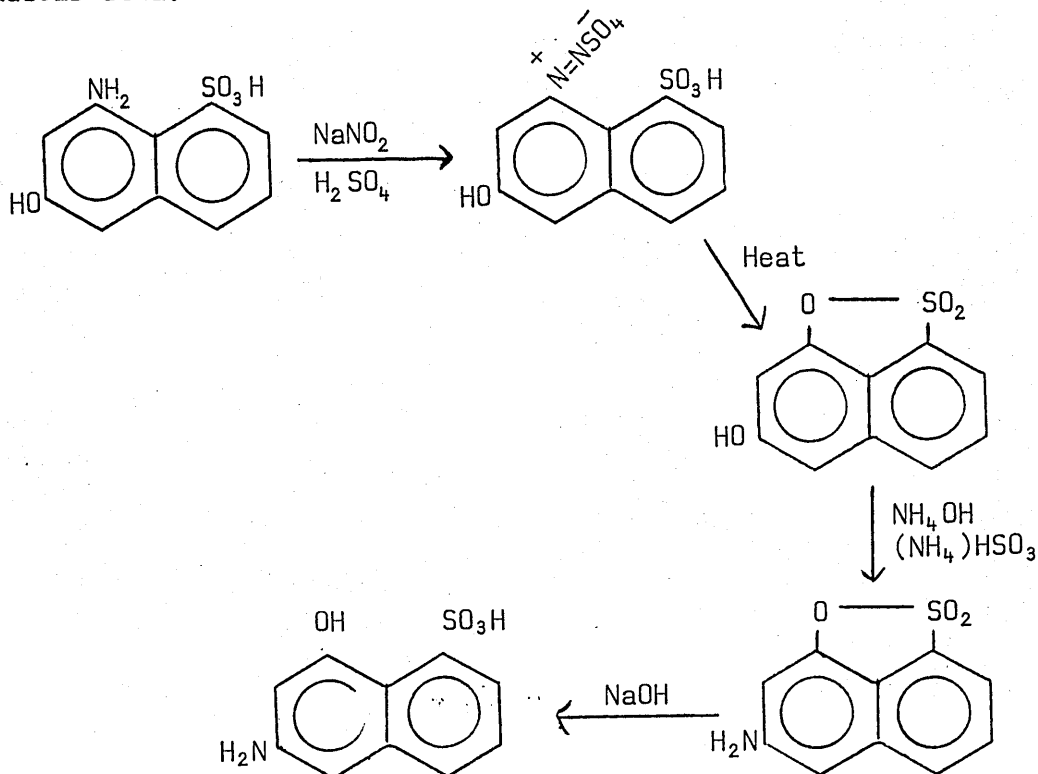


6.10 Isomer 681

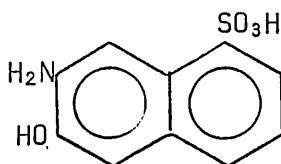


The only method which can be suggested for this isomer is one using Isomer 861 as the base material (Section 6.13). Isomer 861 will be very difficult to make and therefore this method is really only of academic value.

Isomer 861 is charged into dilute sulphuric acid and diazotised by the addition of sodium nitrite. When the diazotisation is complete, the temperature is raised to 100°C when nitrogen will be liberated and the 'Sultone' formed, which is filtered off and washed acid free. The 'Sultone' is then aminated by heating with ammonia and ammonium bisulphite and then hydrolysed by heating with dilute caustic soda.

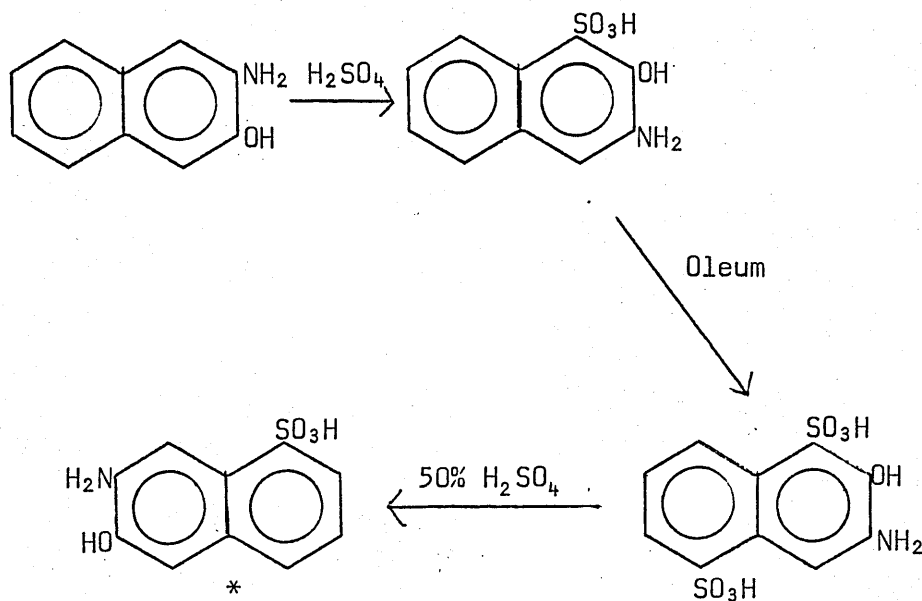


6.11 Isomer 761

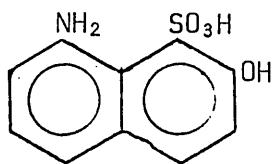


The following method is suggested as a possible route for the preparation of this isomer.

2-Amino-3-hydroxy-naphthalene (16g, 0.1mol) is added slowly to sulphuric acid 96% (200g) at 0-5°C and the mixture stirred for 5 hours. Oleum 25% (220g, .68 mol) is then added over 3 hours at 0-5°C. The mixture is stirred for a further 10 hours at this temperature. The sulphonation mass is then poured into a mixture of ice and water such that the temperature does not exceed 10°C and the acid strength 50%. The temperature is raised to 40°C and stirred until the -1-sulphonic acid group has been eliminated. The mass is then cooled and the isomer filtered off and washed acid free.

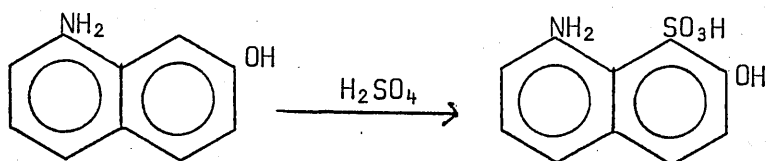


6.12 Isomer 821

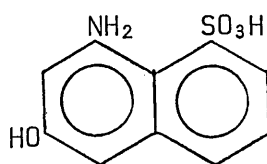


The only method of preparation which can be suggested for this isomer is the sulphonation of 1-amino-7-hydroxy-naphthalene with 90% sulphuric acid 90% at 0-5°C.

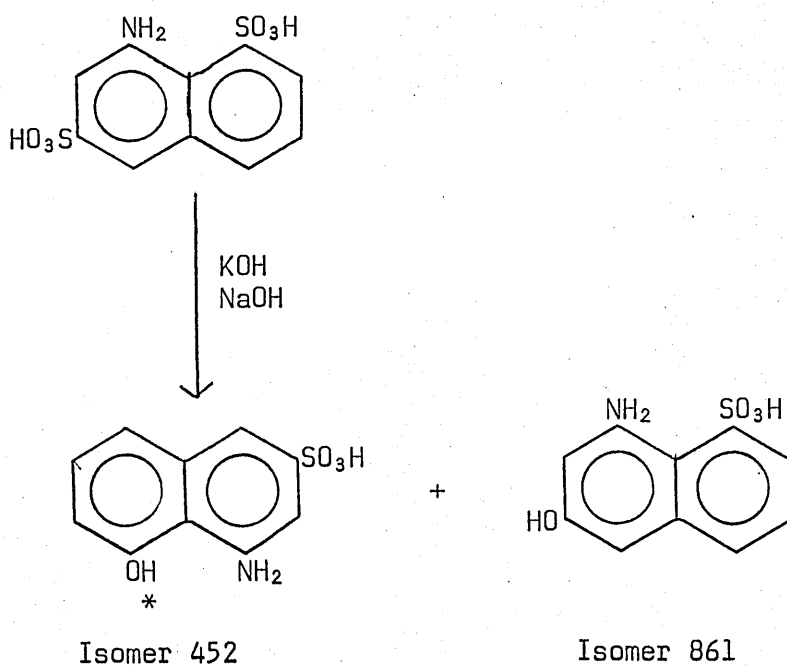
This suggestion is made against literature information that this reaction will give isomer 461⁶⁶ or isomer 462¹¹.



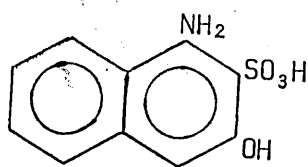
6.13 Isomer 861



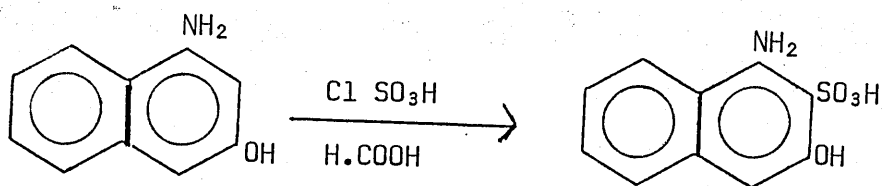
This isomer would be very difficult to prepare. It is thought that if 8-amino-naphthalene-1,6-disulphonic acid (1.3.8. Acid) was fused with a mixture of caustic soda and caustic potash (50 : 50) at 190⁰-200⁰C, some of the isomer would be formed as an impurity in the main product which would be isomer 452.



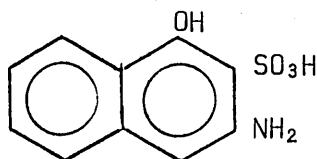
6.14 Isomer 132



The only method which can be suggested for this isomer is the same as was used for Isomer 231 (Section 6.1). The base material would be 1-amino-3-hydroxy-naphthalene, which would be charged into 1,2-dichlorobenzene and sulphonated with chlorosulphonic acid, adding formic acid as a catalyst.¹⁶

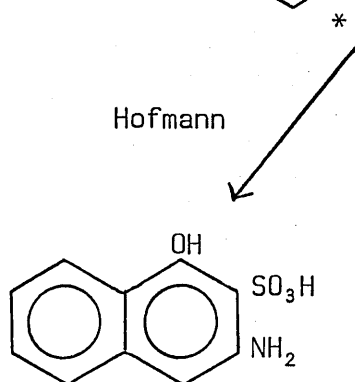
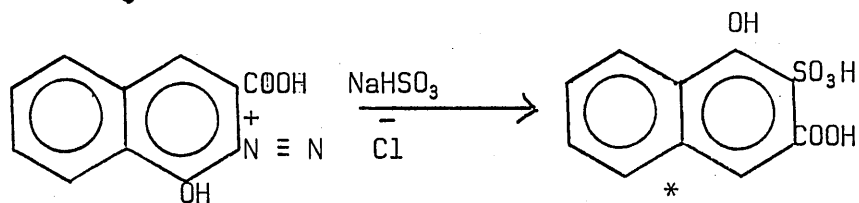
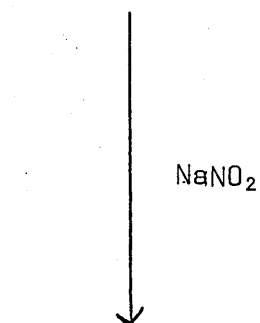
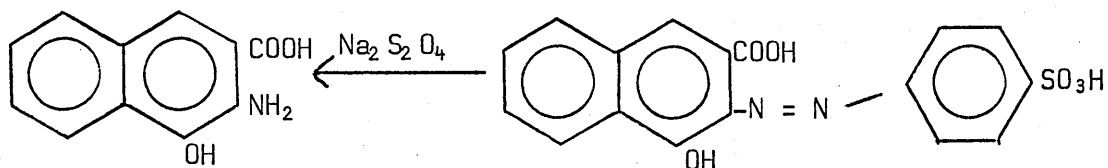
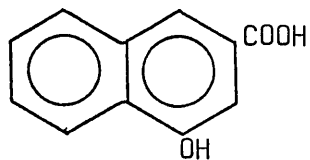
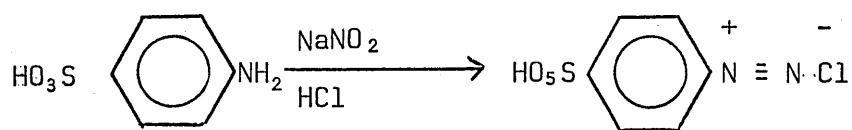


6.15 Isomer 312

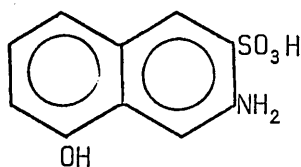


The following method is suggested for the preparation of this isomer:-

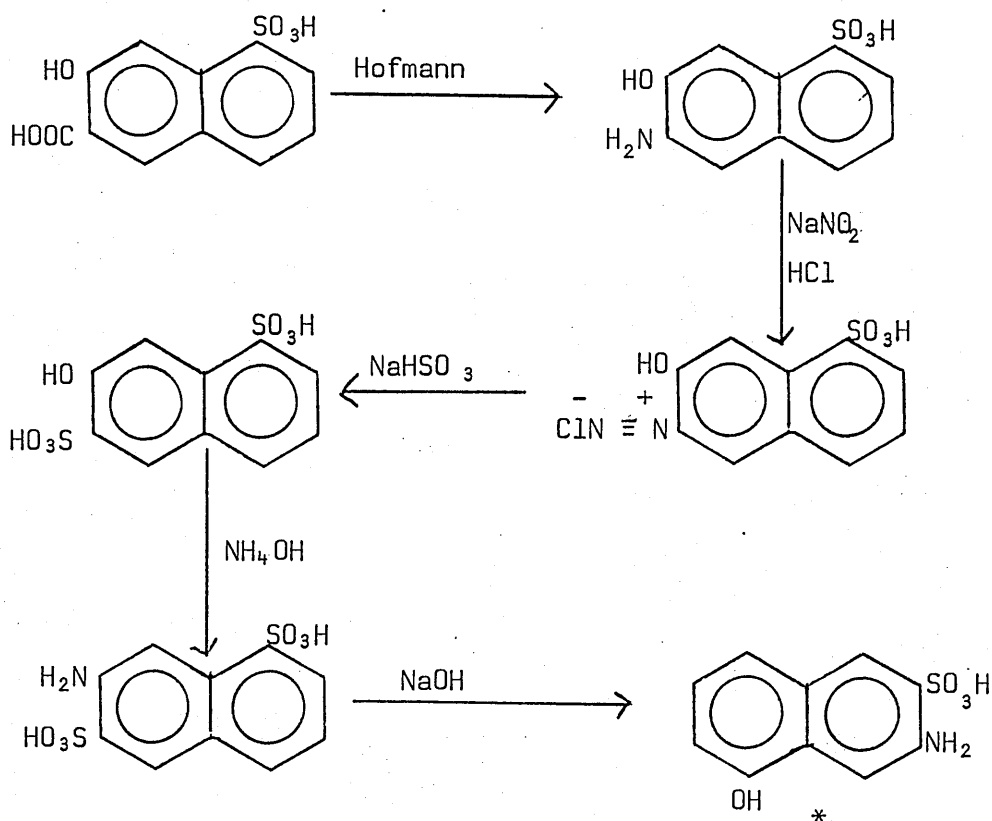
4-Hydroxy-2-naphthoic acid is dissolved in water by the addition of sodium carbonate and then coupled with diazotized sulphanilic acid. The resultant dyestuff is filtered off, charged into water, made strongly alkaline with caustic soda, and the diazo link split by the addition of sodium dithionate. The isolated product would be 3-amino-4-hydroxy-2-naphthoic Acid. The amino group is now diazotised by the addition of sodium nitrite in acid solution and this solution run slowly into excess sodium bisulphite liquor 40% when the diazo group will be replaced by a sulphonic acid group.⁶⁷ The final reaction is to convert the carboxy group to an amine group by the Hofmann reaction.



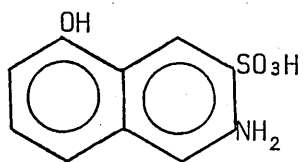
6.16 Isomer 352



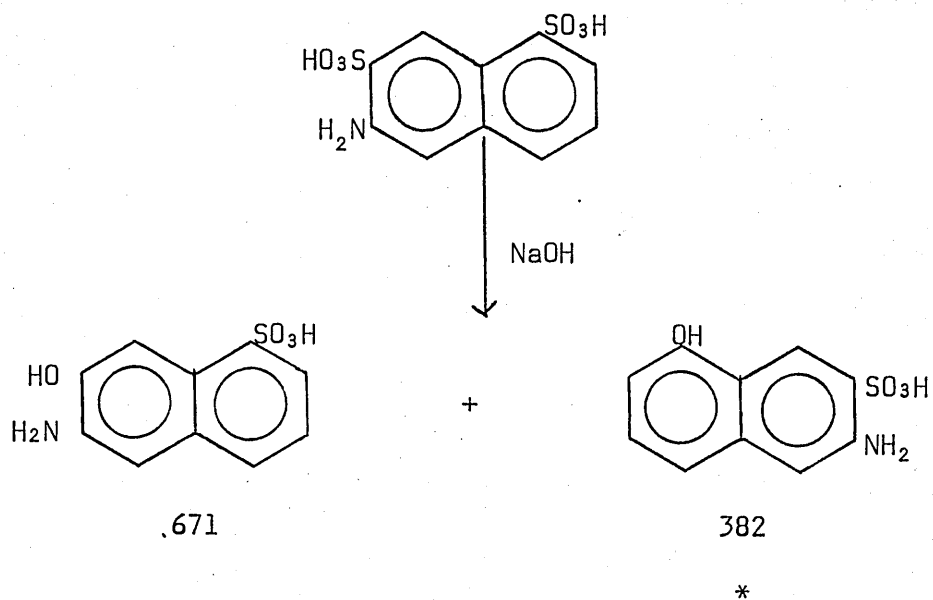
The following method of preparation for this isomer is considered possible. 7-hydroxy-6-carboxy naphthalene-1-sulphonic acid is converted to 6-amino-7-hydroxy naphthalene-1-sulphonic acid by the Hofmann Reaction. This compound in turn is diazotised with sodium nitrite and run into sodium bisulphite solution⁶⁷ 40% to give the 7-hydroxy-naphthalene-1,6-disulphonic acid. This could be aminated by the special method⁶³ to give 7-amino-naphthalene-1,6-disulphonic acid. Fusion with caustic soda 75% at 180-185°C should give the required isomer.



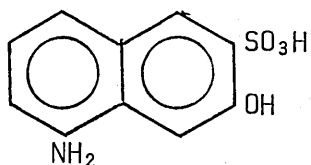
6.17 Isomer 382



The method of preparation of this compound has already been used in Section 6.9 viz. by the caustic fusion of 6-amino naphthalene-1,7-disulphonic acid.⁶⁵



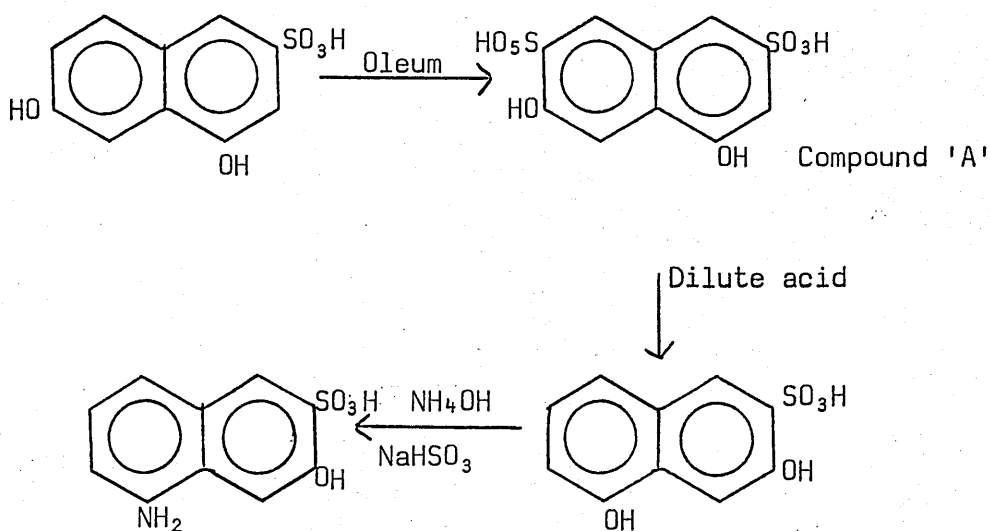
6.18 Isomer 532



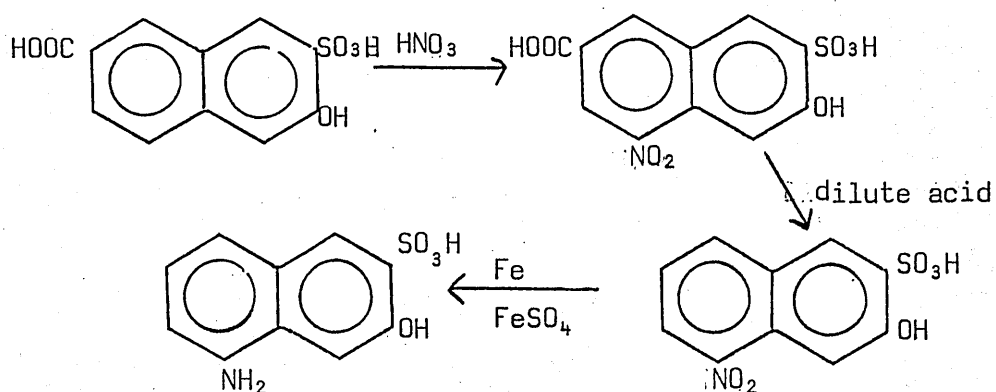
This compound along with Isomer 821 (Section 6.12) are the two unknown sulphonic acids of 1-amino-7-hydroxy-naphthalene. The Author some 35 years ago had a commitment to prepare all the six sulphonic acids of 1-amino-7-hydroxy-naphthalene for research purposes but failed to make these two.⁶⁸

Discussions⁶⁹ on the whole topic and in particular on Isomer 532 were held with Sir Robert Robinson, who advised the Author to try the two following routes.

Route 1

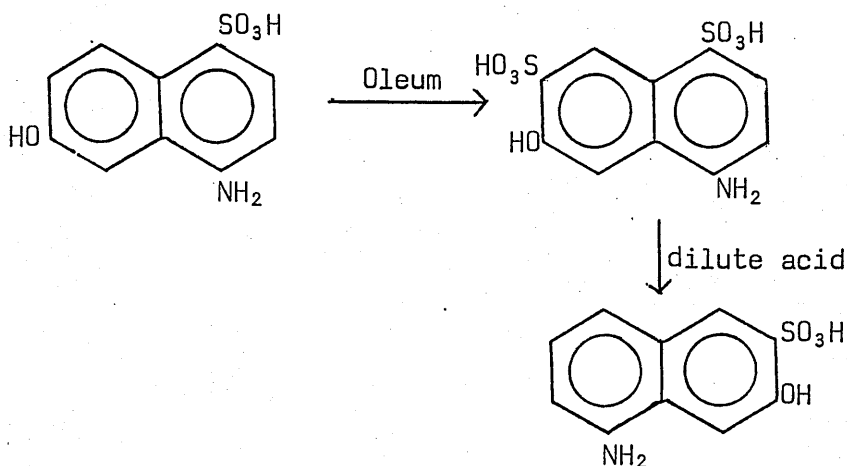


Route 2

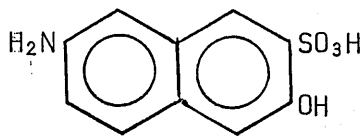


These suggestions were never attempted in the laboratory, because a further literature search^{70,71} revealed that COMPOUND 'A' on heating with sulphuric acid even under the mildest of conditions desulphonated to give 1,7-dihydroxy-naphthalene, and 3-amino-5-hydroxy-naphthalene-2,7-disulphonic acid (2R Acid) behaved similarly. Further the base material for Route 2, 6-hydroxy-2-naphthoic acid was not available.

In considering other methods, Ako Reports¹⁰ stated that the further sulphonation of Isomer 461 was exceptionally difficult but it was thought that this method of obtaining Isomer 532 was worth trying. The method of preparation would then be as follows:-



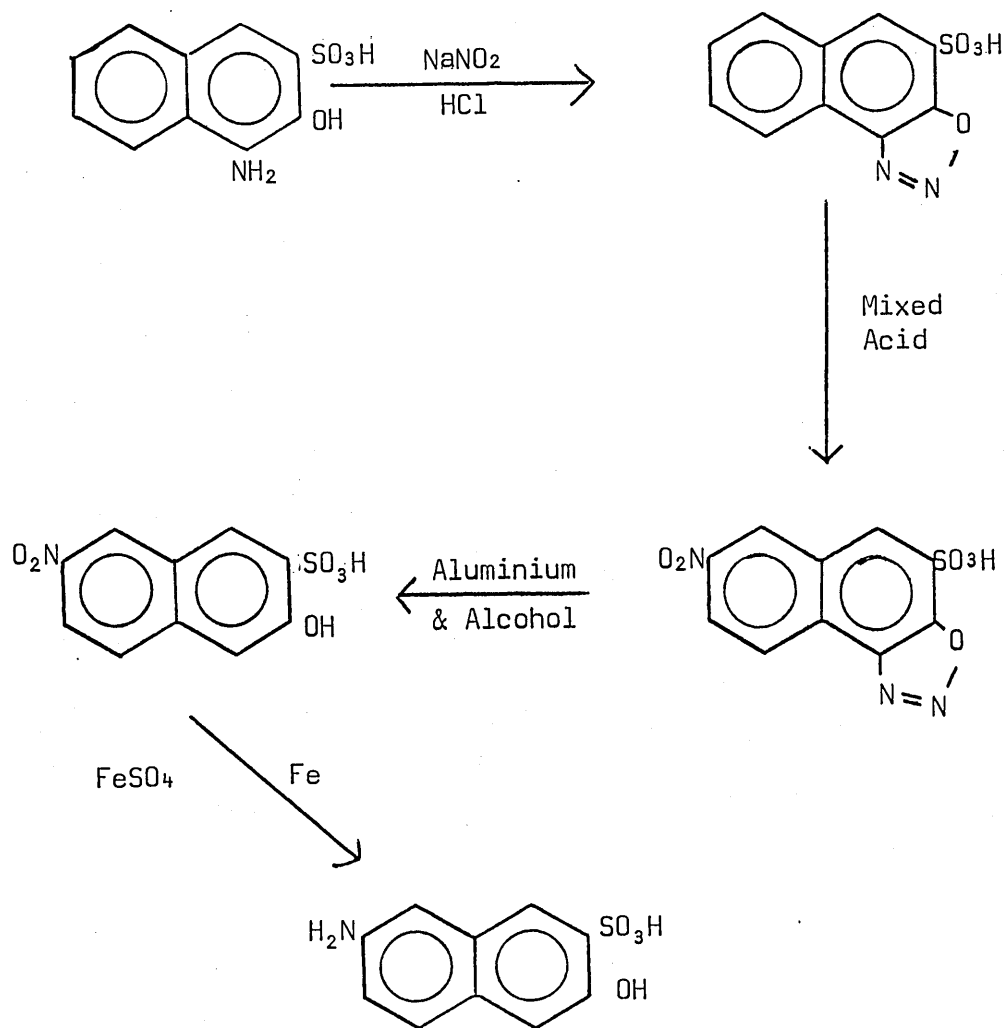
6.19 Isomer 732



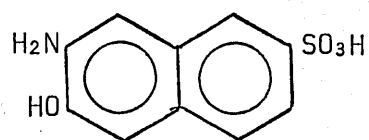
The following method is thought to be practical based on the Author's experience in nitrating diazo compounds and the reported work of Blagney.²³

The details are as follows:-

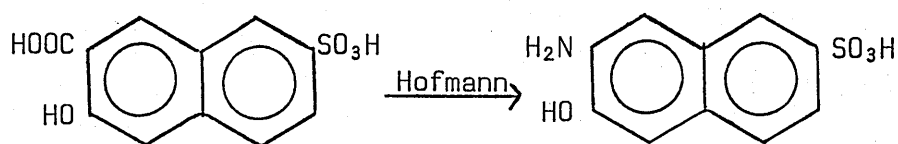
Isomer 432 is diazotised by charging it into dilute hydrochloric acid and adding sodium nitrite. The diazo compound is isolated and dried very carefully. The dried product is then charged into sulphuric acid 100% and stirred for 10 hours. Mixed nitric/sulphuric acid is then added to nitrate the mixture. The resultant compound is then treated with aluminium in alcohol to remove the diazo group forming 7-nitro-3-hydroxy-naphthalene-2-sulphonic acid which is reduced to the required 7-amino-3-hydroxy-naphthalene-2-sulphonic acid by the standard iron-iron salt aqueous procedure.



6.20 Isomer 762



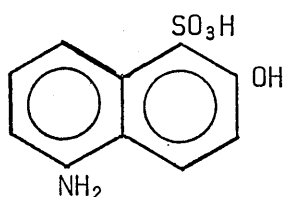
This isomer can be prepared from 6-hydroxy-7-carboxy-naphthalene-2-sulphonic acid,⁷² by subjecting it to a Hofman Reaction.



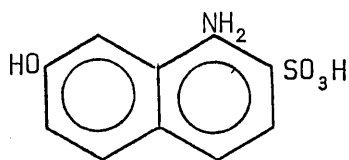
7.0 Experimental Details of Five Unrecorded Isomers

Some 30 years ago the Author prepared in the laboratory some 170 Naphthalene sulphonic acid compounds and their derivatives, and set up a scheme of identification²¹ from which it was possible to deduce a relationship between structure and U.V. fluorescence. Up and until the end of March 1980 when the Author's involvement ceased, every new compound tested fitted into the derived tables.

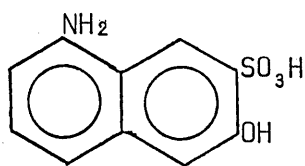
The following isomers have been prepared in the laboratory and their constitution established. None of the isomers have previously been recorded.



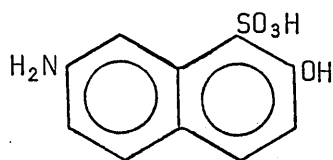
Isomer 521



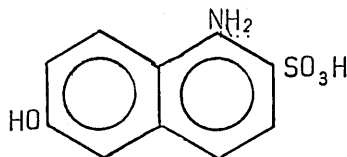
Isomer 172



Isomer 832



Isomer 721



Isomer 162

7.1 Preparation of 5-Amino-2-Hydroxy-naphthalene-1-Sulphonic Acid

(Isomer 521)

Stage 1 Preparation of 1-Amino-6-hydroxy-naphthalene

Caustic potash 92% (1696g, 28mol) was charged into an agitated fusion pot together with caustic soda 98% (163g, 4mol) and water (328g) and heated to 200°C, the agitator being started when the mass became fluid. 5-Amino-naphthalene-sulphonic acid (1,6 Cleve Acid) 89.2% (1000g, 4mol) was charged slowly during 2 hours, the temperature rising to 245°C to maintain fluidity. It was held at 245°C for half an hour, cooled to 200°C and water (1000g) added as quickly as possible. The mass was poured into water (3000g) and the temperature adjusted to 95°C. Hydrochloric acid 36% (3345g, 33mol) was then run in to give a strong permanent blue colour to Congo Red Test Paper when free from sulphur dioxide. The hot solution was filtered to remove impurities, salt added to 10%, cooled to 20°C and the precipitated 1-amino-6-hydroxy-naphthalene hydrochloride filtered and washed with brine 10% (200ml). The hydrochloride was charged into water (2000ml), neutralised with sodium acetate to precipitate the free base, filtered washed with cold water and dried under vacuum at 80-85°C. Yield 311g (49% Theory).

Stage 2 Preparation of Isomer 521

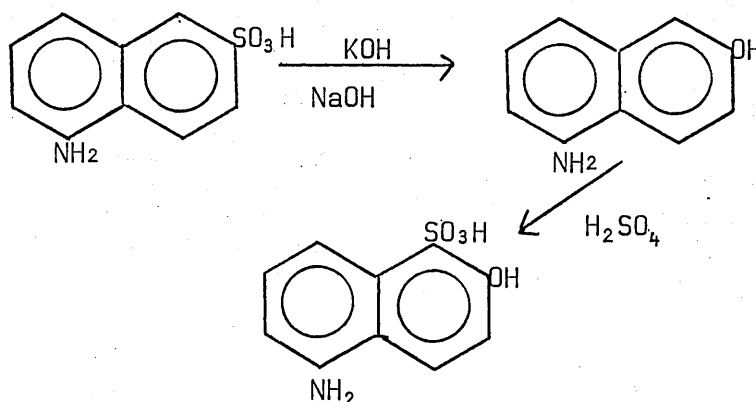
1-Amino-6-hydroxy-naphthalene (95.4g, 0.6mol) was added to sulphuric acid 100% (1000g) at 10-15°C the temperature raised

slowly to 30°C, held at 30°C for two hours, and poured slowly onto ice (2000g). The product was filtered, washed acid free with water, recharged into water (800g) sodium acetate added until the product had dissolved, screened to remove impurities, reprecipitated at 90°C by the addition of hydrochloric acid cooled, filtered, washed with water and dried. Yield 93.4g (65% Theory).

Identification

The product had a bright light green fluorescence under U.V. light which indicated that the sulphonic acid group was in the same ring as the hydroxy group²¹. Boiling with 50% sulphuric acid gave a new product identified as 1-amino-6-hydroxy-naphthalene. The isomer coupled with diazo compounds but did not after acetylating the amino group, which indicated that the coupling was to the amino group and not to the hydroxy group.

The amino group was eliminated by diazotising and boiling with hypophosphorous acid in alcohol and the resultant solution subjected to the Adams Test (Section 4.1.1) which confirmed the 2-hydroxy-naphthalene-1-sulphonic acid (Oxy-Tobias) structure. The compound was therefore the required Isomer 521.



7.2 Preparation of 1-Amino-7-Hydroxy naphthalene-2-Sulphonic Acid (Isomer 172)

Stage 1 Preparation of 4-Amino-naphthalene-1,3,6-trisulphonic acid.

Oleum 25% (1560g, 4.88mol) was run into a glass lined sulphonator and cooled to 15°C. 8-amino-naphthalene-2-sulphonic acid (1,7 Cleve Acid) 100% 446g, 2mol) was added during 2 hours at 15-20°C and heated to 60°C for 4 hours then cooled to 20°C. Oleum 65% (446, 3.62mol) was added during 1 hour at 15-20°C and the mass heated to 85-90°C for 16 hours. It was then poured into 9000g ice and water, salted with salt (800g), cooled to 20°C, filtered and washed with saturated brine. Yield 75%.

When as in this case the isolated product was not required the sulphonation mass was used for the subsequent stage.

Stage 2 Desulphonation to 1-Amino-naphthalene-2,7-disulphonic acid.

The sulphonation mass was poured onto ice and water (2000g) to give a sulphuric acid strength of 45% at 115°C. After holding at 115°C for 4 hours it was diluted with water to 4000ml, cooled to 20°C, filtered, then slurry washed in cold water, filtered and dried. Yield 412g, strength by diazotisation 75.5% (51.5% Theory).

Stage 3 Preparation of Isomer 172

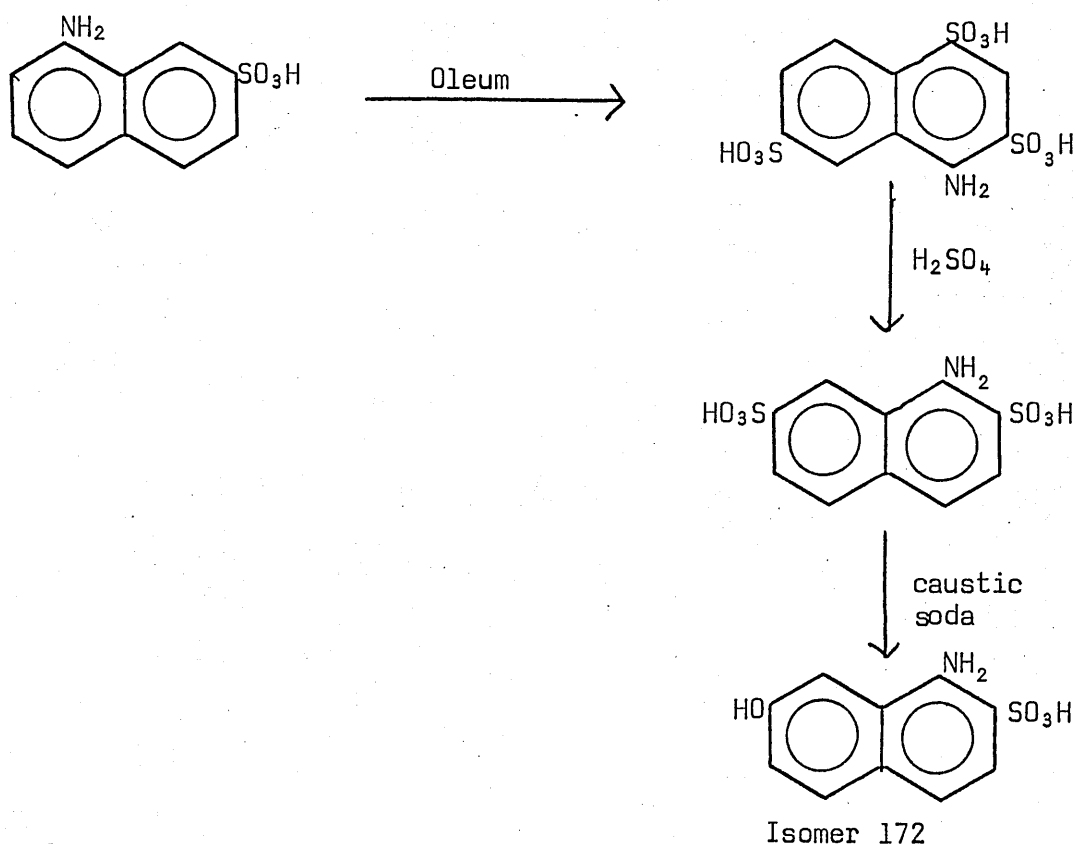
Caustic soda 98% (102g, 2.5mol), ater (204g) and 1-amino-naphthalene-2,7-disulphonic acid 75.7% (148g .33mol) were

charged into an autoclave and heated to 200°C in 4 hours. After holding at 200°C for 12 hours it was cooled, diluted with Water (600ml) and acidified with hydrochloric acid. The sulphur dioxide was boiled off the mass cooled, filtered, redissolved in sodium acetate solution, and screened to remove impurities. The product was reprecipitated with hydrochloric acid and filtered and washed with cold water. Yield 2.0g.

The main loss was due to deamination with the formation of 7-hydroxy-naphthalene-2-sulphonic acid (F.Acid) which was lost in the liquors.

The isomer was identified by eliminating the amino group and confirming the resultant product to be F.Acid.

The U.V. fluorescence was blue indicating the sulphonic acid group to be in the same ring as the amino group.



7.3 Preparation of 1-Amino-6-Hydroxy-naphthalene-2-Sulphonic Acid (Isomer 162)

Stage 1 Preparation of 1-Amino-naphthalene-2,4,6-trisulphonic acid

Oleum 25% (1560g, 4.88mol) was charged into a cast iron sulphonating pot and cooled to 15°C. 5-Amino-naphthalene-2-sulphonic acid (1,6 Cleve Acid) 100% (446g, 2mol) was added during 2 hours at 15-20°C and then heated to 60°C for 4 hours to form 4-amino-naphthalene-1,7-disulphonic acid then cooled to 20°C. Oleum 65% (446g, 3.62mol) was then added during 1 hour at 15-20°C and heated to 95-100°C for 16 hours. After cooling to 20°C the mass was poured into 8000ml cold water, sodium carbonate (106g, 1mol) added, and the sodium salt limed out with lime (1600g). The gypsum was filtered off, well washed with boiling water, and the filtrates and washings evaporated to 3500ml. The product was isolated by the addition of hydrochloric acid 36% (500ml), and salt (200g), cooled to 20°C filtered and washed with brine 25% (500ml) and dried. Yield 573g @ 70.2% (52.5% Theory).

Stage 2 Preparation of 1-Amino-naphthalene-2,6-disulphonic acid

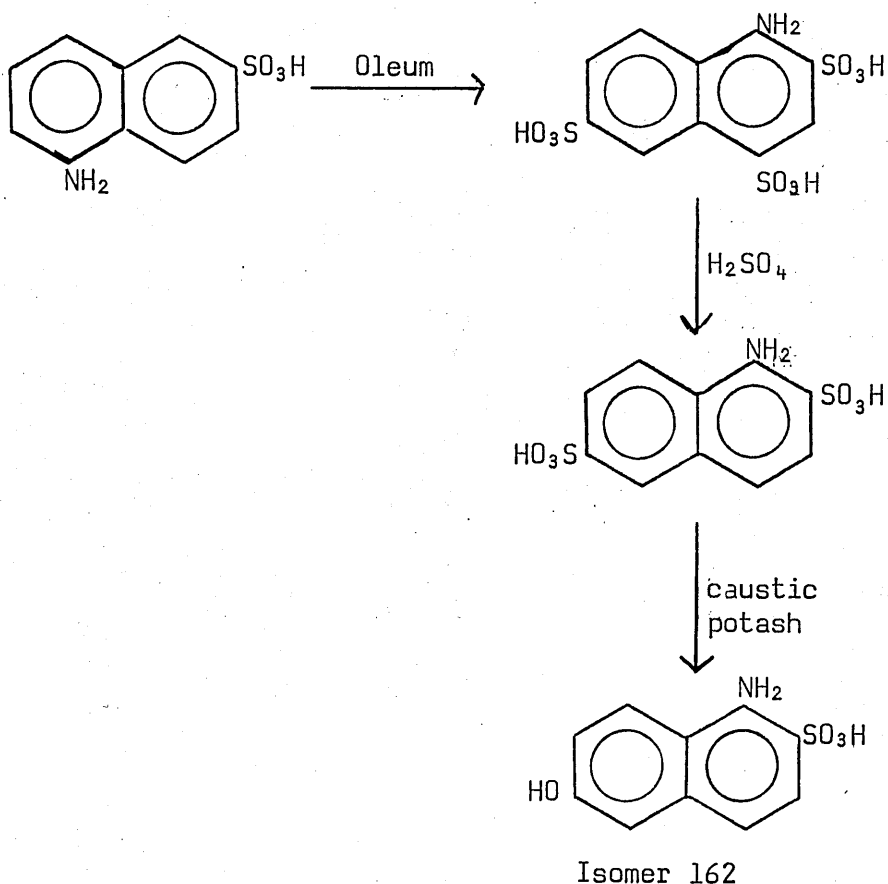
Sulphuric acid 48% (3000g) was charged to a glass flask and heated to 50°C, 1-amino-naphthalene-2,4,6-trisulphonic acid 70.2% (545g, 1mol) added and heated at reflux (118-120°C) for 6 hours, cooled, & filtered. The product was redissolved in dilute caustic soda solution, screened to remove impurities and reprecipitated at 90°C with hydrochloric acid 36%, filtered and

washed acid free with cold water. Yield 79g (Theory 30.5% as mono sodium salt).

Stage 3 Preparation of 1-Amino-6-hydroxy-naphthalene-2- sulphonic acid
(Isomer 162)

Caustic potash 92% (300g, 4.93mol), water (100ml) were charged to an agitated fusion pot and heated to 150°C. 1-Amino-naphthalene-2,6-disulphonic acid mono sodium salt 100% (101g, .25mol) was charged at 150-170°C in 2 hours and heated at 210-220°C for 4 hours. The mass was then diluted with water (200ml), and then poured into water (1500ml) and acidified with hydrochloric acid. After cooling to 20°C it was filtered and washed with cold water. Yield 19g (Theory 28.4%)

The product was identified by the usual procedure.



7.4 Preparation of 8-Amino-3-Hydroxy naphthalene-2-Sulphonic Acid (Isomer 823)

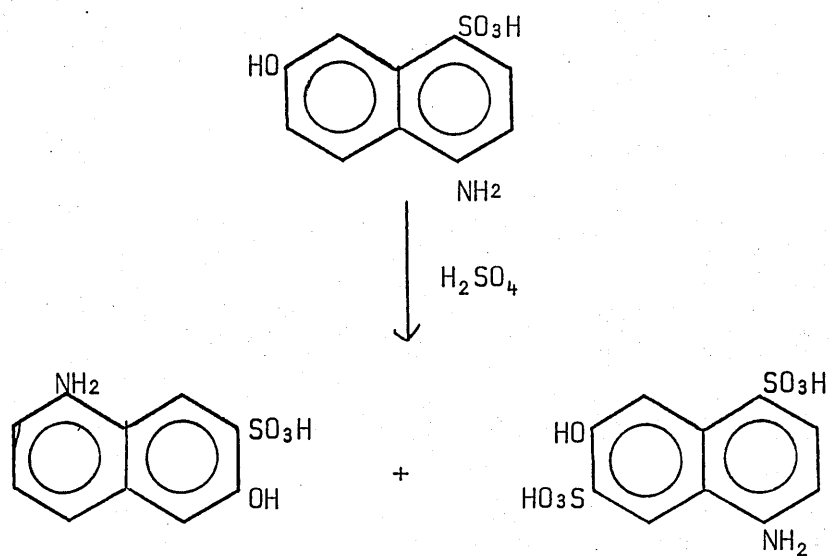
Method 1

1-Amino-6-hydroxy-naphthalene (see Section 7.1) (10g) was added to sulphuric acid 90% (100g) at 15-20°C during half an hour. After heating to 120°C for 2 hours it was cooled to 25°C and poured into ice (100g), filtered and washed acid free with cold water. It was redissolved in sodium acetate solution at 90°C, screened and the filtrate cooled to 20°C when the sodium salt of Isomer 832 crystallised out and was filtered washed and dried. Yield 3g.

Method 2

"Sulphuric acid 100% (300g) was charged to a reaction flask and heated to 20°C. 4-amino-7-hydroxy-naphthalene-1-sulphonic acid (Isomer 471) 100% (48.2g, .2mol) was added and heated to 95°C for 10 hours, then poured into water (2000ml). Sodium carbonate (10.7g, .202mol) was then added and the solution neutralised to Brilliant Yellow Test Paper by the addition of lime. The gypsum was filtered off, washed with boiling water, and the filtrates and washings evaporated to 2000ml. The product was filtered off, redissolved in sodium acetate solution at 90°C, screened, cooled to 20°C and the insoluble sodium salt filtered off. This was then added to water and the free acid compound precipitated with hydrochloric acid, cooled, filtered and washed acid free with cold water. Yield 10g.

From the filtrates was isolated 4-amino-7-hydroxy-naphthalene-1,6-disulphonic acid (35g) which was also an unknown compound.

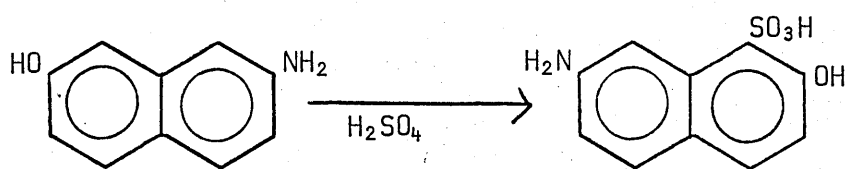


Isomer 832

7.5 Preparation of 7-Amino-2-Hydroxy-naphthalene-1-Sulphonic Acid
(Isomer 721)

Sulphuric acid 90% (250g) was charged into a reaction flask and cooled to 10-15°C. 2-Amino-7-hydroxy-naphthalene (25g) was added slowly with agitation during half an hour and the agitation continued for 3 hours at 10-15°C. The sulphonation mass was then poured into ice (300g), the product filtered off, and washed acid free with ice cold water. It was then recharged into water (150ml) and dissolved by adding sodium acetate, screened from impurities and reprecipitated by adding hydrochloric acid. The product was filtered, washed with cold water and dried. Yield 18g.

This product was identified by subjecting to the usual system of analysis of deamination and comparing with all the hydroxy-naphthalene-1-sulphonic acids and confirming the Oxy-Tobias formula by the Adams Test (Section 4.1)



8.0 Discussion of Results

Nothing was found in the literature which gave any indication that the field of Amino Hydroxy Naphthalene Sulphonic Acids was about to resurge with or without products made from as yet unknown or non-manufactured isomers. All the recent references of process improvements were for the established 1.2.4 Acid, γ , J, and S, Acids, with M.Acid being virtually forgotten.

The work of Blagney²³ could be described as progressive, being an extension of the 1.2.4.Acid process, but he ignored what could have been the most commercial compound i.e. 7-nitro-naphth(1,2)-oxadiazole-8-sulphonic acid (Section 4.5) by treating it only as an intermediate to produce Isomer 372.

From a commercial point of view, Blagney should have compared its properties with 7-nitro-naphth-(1,2)-oxadiazole-5-sulphonic acid (commercially made by nitrating Diazo 1.2.4 Acid) and then substituting it for the latter in the preparation of dyestuffs etc. when exciting properties could have emerged.

The works of Roe¹⁵, Thiot¹⁵, Jarkovsky¹⁹, Osman³⁰, Baman^{39,40}, Schriever^{39,40,41}, Nickel¹⁴ and Suckful¹⁴ at first glance were exciting and would certainly be to students and to chemists making one-off preparations in the laboratory but they offered little or nothing to the would-be manufacturer because all the works were concerned with the final stages of the reactions often using base materials which were not readily available. The novelty of the reactions was interesting but not very commercial.

One impression derived from preparing this review is that there is a vast amount of detailed knowledge and expertise which is known to industry but will be lost in time because it has never been published. Some of this information refers to actions so simple that they are not considered worthy of recording yet are of paramount importance. Such an example is given as a note in Section 5.2.2 concerning the physical form of gypsum. Even this note may not be entirely satisfactory since it does not emphasise that the bad physical form resulting from the addition of too much alkali cannot be reversed by readjusting the pH to 3-6.5. A further example is given in Section 5.3.1 referring to the isolation of Amido J. Acid; this states that the mass is cooled to 20°C, filtered and washed with dilute acid. From the Author's experience if this was performed as stated, which would imply full cooling water on the coils, an almost impossible situation would result; the Amido J. Acid would precipitate on the coils and then the heat transfer would become nil. If by some means the cooling did occur, the physical form would be like porridge and would therefore not filter. The strength of the acid wash is not disclosed, so the loss of yield at this stage could be very large. Such information is an essential tool of the manufacturer but not of the laboratory chemist.

There is one particular facet which is a source of concern, that is the somewhat casual abstracting of some of the papers.²³ This has already been discussed in Section 4.5 but calls for further comment. Nitrations are dangerous reactions, and inaccurate abstracting of the preparation details could be very serious to the unskilled chemist. Even the common sense instruction 'The mass

was constantly stirred' should never be omitted. In Section 4.2 Bayer describes the use of 5-nitro-naphthalene-1-sulphonic acid which is produced by the addition of aqueous nitric acid to the stirred sulphonation mass of naphthalene-1-sulphonic acid. This nitration which could be thought to be so simple, is very hazardous in the initial stages, and should the agitation stop, very dangerous. Such so called minor details are of vital importance.

A further example of this is the recorded process of M.Acid (Section 5.5) when the term 'Acidified at 80°C' was used; and in section 5.3 the term 'The product was isolated by acidifying with sulphuric acid'. The former should have read 'Acid was run in at 80°C to isolate the M.Acid whereas the latter should have stated that the product was isolated by running the diluted fusion mass into excess sulphuric acid and in both cases that sulphur dioxide was liberated. This latter procedure of running the diluted fusion mass into excess acid is a procedure in Naphthalene Chemistry which if not followed would give low yields i.e. γ Acid and J.Acid and in some special cases i.e. the preparation of dihydroxy-naphthalene compounds, no yield at all.

The high point of this review is undoubtedly the work recorded in the Japanese Patent⁶¹ describing the fusion of naphthalene-1,3,6-trisulphonic acid to 4,7-dihydroxy-naphthalene-2-sulphonic acid which could then be aminated to J.Acid. As stated in Section 5.3.7 the information can be seriously questioned, but if the Author was asked to write a programme of work on the outcome of this review, the investigation of this information would be the No. 1 choice with the second choice being the follow up of the work of Arai⁵³ i.e.

sulphonating with SO_3 in Sulfolane or other solvents to try and obtain a simple naphthalene-sulphonic acid rather than the usual mixture of isomers.^{1,2}

The overall assessment of this review is that the halcyon days of Naphthalene Chemistry have slipped away and there is at the present time no urgent requirement for the improvement of the 'Big Five' or to obtain new isomers. Amino-hydroxy-naphthalene-sulphonic acids are produced by multi-stage processes in large and expensive plants and it is difficult to envisage a resurgence of this branch of chemistry.

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